APPENDIX A

Quality Assurance Project Plan

Prepared for

Settling Work Defendants

QUALITY ASSURANCE PROJECT PLAN

OMEGA SUPERFUND SITE
OPERABLE UNIT 2

Prepared by

Geosyntec consultants

engineers | scientists | innovators

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Project Number: WR2209

18 November 2016

Quality Assurance Project Plan

Omega Superfund Site

Operable Unit 2

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18 November 2016

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LIST OF ACRONYMS, ABBREVIATIONS, AND COMMON TERMS

2010 RI	August 2010 OU2 Remedial Investigation
2011 ROD	OU2 Interim Action Record of Decision, dated September 20, 2011
2016 CD	Consent Decree lodged April 20, 2016 covering Operable Unit 2 at the Omega Chemical Corporation Superfund Site
A	Measured value of the analyte after spike is added
C	Percent Completeness
Calscience	Eurofins Calscience Environmental Laboratories, Inc.
CDM	CDM Smith, Inc.
CE Area	Central extraction area (The location of the CE area is depicted in the 2016 CD, Appendix C as the area between the NE and Telegraph Road.)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
CLP-SOW	Contract Laboratory Program Statement of Work
CMP	Compliance Monitoring Plan
COCs	Chemicals of Concern
COPCs	Chemicals of Potential Concern
D1	First sample value
D2	Second sample value (duplicate)
Day	Day means a calendar day unless expressly stated to be a working day. A working day is a day other than a Saturday, Sunday, or federal or state holiday.
DO	Dissolved Oxygen
DOT	Department of Transportation
DQOs	Data Quality Objectives
DTSC	California Department of Toxic Substances Control

DVR	Data Validation Report
EDD	Electronic Data Deliverable
EPA	United States Environmental Protection Agency
FSP	Field Sampling Plan
Geosyntec	Geosyntec Consultants, Inc.
H+A	Hargis and Associates, Inc.
HASP	Health and Safety Plan
ICs	Institutional Controls. (ICs are non-engineering controls that will supplement engineering controls to prevent or limit potential exposure to hazardous substances, pollutants, or contaminants at the Site related to the Work and to ensure that the portion of the ROD applicable to the Work is effective.)
ICV	Initial Calibration Verification
IDW	Investigation-Derived Waste
Key Treatment Constituents	Treatment constituents that may require treatment to meet discharge requirements associated with end-use (reinjection, spreading basin, reclaim). The Key Treatment Constituents are considered during the RD based on end use.
LCS/LCSD	Laboratory Control Sample/Laboratory Control Sample Duplicate
LE Area	Leading Edge Area of OU2 is the area in the 2016 CD, Appendix C that is south of the CE Area
LEI	Leading Edge Investigation
LEIWP	Leading Edge Investigation Work Plan
Main COCs	13 COCs identified in the ROD as “main COCs” and listed in Table 2. Includes eleven VOCs, 1,4-dioxane, and hexavalent chromium. The Main COCs are included in the COC list for the RD.MCLs Maximum Contaminant Levels
MCLs	Maximum Contaminant Levels (EPA and California)
MCS	Method Control Sample

MDL	Method Detection Limit
MS/MSD	Matrix Spike/Matrix Spike Duplicate
n	number of replicates
NBS	National Bureau of Standards
NE Area	Northern extraction area (The location of the NE area is depicted in Appendix C of the 2016 CD as an area north of the CE)
NE/CE Area	A portion of the area of the groundwater contamination identified by EPA as OU2 in its 2011 ROD. The NE/CE Area is bounded by the OU2 boundary as depicted in the 2016 CD, Appendix C and the area north of Telegraph Road. It includes the NE and CE areas as depicted in the ROD as well as the northern portion of the LE area as depicted in the ROD.
NELAP	National Environmental Laboratory Accreditation Program
NL	Notification Level, California State Water Resources Control Board
Omega	Omega Chemical Corporation
Omega Property	The property formally owned by the Omega Chemical Corporation, encompassing approximately one acre, located at 12504 and 12512 East Whittier Blvd, Whittier, California. OU1 and OU3 are addressing soil, groundwater, and soil vapor source control at the Omega Property.
OU2	Operable Unit 2, the contamination in groundwater generally downgradient of Omega Property, much of which has commingled with chemicals released at other locations into a regional plume containing multiple contaminants which, when considered in total, is more than four miles long and one mile wide. The OU2 boundary is depicted in the 2016 CD, Appendix C.
PARCCS	Precision, Accuracy, Representativeness, Completeness, Comparability, and Sensitivity
PC	Project Coordinator, an individual who represents the SWDs and is responsible for overall coordination of the Work. PDI Pre-Design Investigation

PDIWP	Pre-Design Investigation Work Plan
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
R	Percent Recovery
RCRA	Resource Conservation and Recovery Act
RD	Remedial Design (Remedial Design means those activities to be undertaken by Settling Work Defendants to develop the final plans and specifications for the Remedial Action pursuant to the Remedial Design Work Plan.)
RDWA	Remedial Design Work Area. (The RDWA consists of the NE/CE Area and includes potential treated water end use locations that may be adjacent to or outside of OU2.)
RL	Method Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
RWQCB-LA	Regional Water Quality Control Board, Los Angeles Region
s	Standard Deviation
Site	Omega Chemical Corporation Superfund Site, originally listed on the National Priorities List on January 19, 1999, which is located in Los Angeles County, California, and includes the contamination being addressed by multiple Operable Units.
SOPs	Standard Operating Procedures
SOW	Statement of Work, Appendix B to the 2016 CD.
STLC	Soluble threshold limit concentration
Supervising Contractor	The entity selected by SWDs to oversee field work.
SVOCs	Semivolatile Organic Compounds

SWDs	Settling Work Defendants, as identified in Appendix E to the 2016 CD. SWDs include the McKesson Corporation and OPOG (Omega Chemical Corporation Superfund Site Potentially Responsible Party Organized Group).
T	value of the spike; total number of measurements
TCLP	Toxicity characteristic leaching protocol
TDS	Total dissolved solids
TTLC	Total threshold limit concentration
V	number of measurements judged valid
VOCs	Volatile Organic Compounds
WAMP	Work Area Monitoring Plan
Work	All activities and obligations the SWDs are required to perform under the 2016 CD, except the activities required under the Retention of Records section of the 2016 CD.
Work Area	The portions of OU2 that are the subject of Work under the 2016 CD and the SOW.
Waste Material	Shall mean (1) any "hazardous substance" under Section 101(14) of CERCLA, 42 U.S.C. § 9601(14); (2) any pollutant or contaminant under Section 101(33), 42 U.S.C. § 9601(33); (3) any "solid waste" under Section 1004(27) of RCRA, 42 U.S.C. § 6903(27); or as any of the foregoing terms are defined under any appropriate or applicable provisions of California law.
X	measured value of analyte concentration in sample before the spike is added
y	mean of replicate analyses
y_i	measured value of the i^{th} replicate

LIST OF ADDITIONAL ACRONYMS AND ABBREVIATIONS

1,1-DCA	1,1-Dichloroethane
1,1-DCE	1,1-Dichloroethene
1,1,1-TCA	1,1,1-Trichloroethane
1,2-DCA	1,2-Dichloroethane
1,2,3-TCP	1,2,3-Trichloropropane
cis-1,2-DCE	cis-1,2-Dichloroethane
Freon 11	Trichlorofluoromethane
Freon 113	1,1,2-Trichloro-1,2,2-trifluorethane
NDMA	N-Nitrosodimethylamine
PCE	Tetrachloroethene
TCE	Trichloroethene

1. INTRODUCTION

1.1 General

This Quality Assurance Project Plan (QAPP) was prepared by Geosyntec Consultants, Inc. (Geosyntec) on behalf of the Settling Work Defendants (SWDs) for the Omega Chemical Corporation Superfund Site, Operable Unit 2 (OU2). This QAPP was prepared in accordance with Section 7.7(d) of the Statement of Work (SOW), Appendix B of the Consent Decree (2016 CD) for OU2 at the Omega Chemical Corporation Superfund Site (United States Environmental Protection Agency (EPA), 2016). This QAPP applies to the activities to be performed for the Work Area, consisting of the Remedial Design Work Area (RDWA) and the Leading Edge (LE) Area, within OU2 during the design of the Northern Extraction/Central Extraction Area (NE/CE Area) remedy.

The purpose of this QAPP is to outline specific quality assurance/quality control (QA/QC) procedures such that data collected for the project meet project Data Quality Objectives (DQOs) and are of acceptable quality to meet SWDs' project needs and EPA requirements. This QAPP was written under guidance provided by EPA, *Requirements for Quality Assurance Project Plans*, (QA)/R-5, EPA/240/B-01/003 (EPA, 2006c), *Guidance for Quality Assurance Project Plans*., QA/G-5, EPA/240/R 02/009 (EPA, 2002); and *Uniform Federal Policy for Quality Assurance Project Plans*, Parts 1-3, EPA/505/B-04/900A through 900C (EPA, 2005).

1.2 Purpose

This QAPP describes the QA/QC procedures that will be performed during the course of the work activities set forth in the Pre-Design Investigation Work Plan (PDIWP) (H+A, 2016), the Leading Edge Investigation Work Plan (LEIWP) (Geosyntec, 2016a), and the Work Area Monitoring Plan (WAMP) (Geosyntec, 2016b), which are described further in Section 2 below. Routine application of procedures for obtaining prescribed standards of performance in the monitoring and measuring process, as well as tracking, reviewing, and auditing, will be implemented such that project work is performed in accordance to applicable standards, regulations, and guidelines in support of the project DQOs.

The procedures to ensure the precision, accuracy, and completeness of new data generated during the course of work activities are included in this QAPP, along with the

requirements set forth in EPA's regulations and guidance documents. Also, this QAPP provides the QA requirements for data handling during all phases of the project.

Technical project personnel will incorporate QC samples and quality control checks into field sample data collection, field data analyses, tabulation, computations, and interpretation. Equipment used to perform field measurements will be maintained and calibrated in accordance with the established procedures described in the Field Sampling Plans (FSPs) for the PDI activities (H+A, 2016), LEI activities (Geosyntec, 2016a), and WAMP activities (Geosyntec, 2016b). The records for these activities will be kept and appropriately filed. Internal QC of project deliverables will be addressed by the Project Coordinator (PC), QA Manager, and Quality Management personnel. Quality assurance of project activities will be maintained through periodic audits (Section 11).

1.3 Data Quality Objectives

In accordance with the SOW (Section 7.7 (d)), the data quality objectives were identified through the DQO process which follows EPA *Guidance on Systematic Planning Using the Data Quality Objectives Process*, EPA QA/G-4 (EPA, 2006a). The DQOs for each activity covered by this QAPP are detailed in Section 4 and in Tables 1a through 1c.

1.4 Quality Assurance Project Plan Organization

The organization of the following elements of this QAPP is as follows:

- Section 2 presents the project background, main chemicals of concern (Main COCs), and planned activities covered by this QAPP;
- Section 3 presents project staffing and responsibilities;
- Section 4 presents project QA objectives and DQOs;
- Section 5 presents sampling procedures;
- Section 6 presents documentation and recording procedures;
- Section 7 presents equipment operation and calibration procedures;
- Section 8 presents analytical procedures;

- Section 9 presents data reduction, validation, and reporting procedures;
- Section 10 presents data management procedures;
- Section 11 presents audit procedures;
- Section 12 presents corrective action procedures; and
- Section 13 lists references used in preparing this report.

2. BACKGROUND

2.1 Site Overview

OU2 of the Omega Chemical Superfund Site addresses contamination in groundwater generally downgradient of the Omega Property, much of which has commingled with chemicals released at other locations into a regional plume containing multiple contaminants which, when considered in total, is more than four miles long and one mile wide. The 2011 ROD addresses containment of OU2 groundwater contamination. The Work covered by the SOW includes groundwater containment in the NE/CE Area as well as additional investigation in the LE Area. Source control at the former Omega Chemical Corporation facility in Whittier, California has been addressed under Operable Unit 1 (OU1) and Operable Unit 3 (OU3). Since 2001, the Omega Chemical Corporation Superfund Site Potentially Responsible Party Organized Group (OPOG) has led the investigation and remediation of the former Omega Property under OU1 and OU3 with EPA oversight. In addition to a 1995 removal action, source area remediation has also included groundwater and soil vapor extraction systems which began operating in 2009. McKesson Corporation has worked with California Department of Toxic Substances Control (DTSC) and has undertaken source control actions at its source property located on Sorensen Avenue. On December 7, 2015, the DTSC approved McKesson Soil Remedial Action Closure Report and determined the soil remediation portion of the project was complete. Other source properties contributing to groundwater contamination that has commingled with groundwater contamination from the Omega Property and the McKesson property have been addressed, are currently being addressed, or will be addressed by the DTSC or the Regional Water Quality Control Board, Los Angeles Region (RWQCB-LA) through investigations and source control actions. These activities are important for the future cleanup of OU2 but are not part of the current SOW.

2.2 Groundwater Chemistry

Routine groundwater sampling has been conducted by various parties in and adjacent to the RDWA. Groundwater monitoring in OU2 has focused on constituents that have been detected at concentrations exceeding their screening levels (federal or California maximum contaminant levels [MCLs] and notification levels [NLs]) and have been grouped in five categories: volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), emergent compounds, metals, and general chemistry.

There were multiple VOCs that exceeded screening levels. The sources of the VOCs appear to be related to multiple sites within and adjacent to OU2. The 2010 RI Report identified VOCs that exceeded screening levels and the 2011 ROD identified eleven VOCs that are part of the Main COCs for OU2.

There was only one SVOC that was reported above the screening level (bis(2-ethylhexyl)phthalate). It is suspected that the detections are due to sampling activities and are not representative of groundwater conditions in OU2 (CH2M Hill, 2010). However, since bis(2-ethylhexyl)phthalate was detected above its screening level, this analyte was considered a chemical of potential concern (COPC) for OU2 in the 2010 RI Report. The 2011 ROD included bis(2-ethylhexyl)phthalate in the lists of treatment standards for treated groundwater end use, but did not include it as a Main COC.

Emergent compounds (1,4-dioxane, 1,2,3-trichloropropane [1,2,3-TCP], N-nitrosodimethylamine [NDMA], perchlorate, and hexavalent chromium) were detected at concentrations exceeding their respective screening levels. Therefore, each of these emergent compounds was considered a COPC for OU2 in the 2010 RI Report. The compounds 1,4-dioxane, 1,2,3-TCP, perchlorate, hexavalent chromium and NDMA were suspected to be related to one or more operations within OU2. The 2011 ROD included 1,4-dioxane and hexavalent chromium in the list of Main COCs, but did not list the remaining emergent compounds.

Aluminum, antimony, arsenic, total chromium, manganese, mercury, nickel, selenium, thallium, and vanadium were detected at concentrations exceeding their respective screening levels, and were therefore considered COPCs for OU2 in the 2010 RI Report. Some of detected metals could be naturally occurring but industrial sources located within OU2 may have also contributed to these metals exceedances given that various industrial sources used these compounds (including total chromium and arsenic). The 2011 ROD included hexavalent chromium as a Main COC, and included aluminum, manganese, total chromium and selenium in one or both lists of treatment standards for treated groundwater end use.

General chemistry parameters have also been assessed in OU2 and several general chemistry parameters have been detected in exceedance of screening levels (e.g. total dissolved solids [TDS], nitrate and sulfate). The majority of general chemistry detections represent background (or natural) conditions in groundwater. The ROD did

not include any of the general chemistry constituents as Main COCs, but did include TDS, nitrate and sulfate in the lists of treatment standards for treated groundwater end use.

2.2.1 Constituents

The 2011 ROD identified 13 COCs for OU2, eleven of which are VOCs (tetrachlroethene [PCE], trichloroethene [TCE], Freon 11, Freon 113, 1,1-dichloroethene [1,1-DCE], cis-1,2-dichloroethene [cis-1,2-DCE], chloroform, carbon tetrachloride, 1,1-dichloroethane [1,1-DCA], 1,2-DCA, and 1,1,1-trichloroethane [1,1,1-TCA]); one is an inorganic constituent (hexavalent chromium) and the remaining compound is 1,4-dioxane (Table 2). As indicated previously, these 13 COCs will be referred to as Main COCs in the RD documents and are included in the COCs for the purpose of the RD. Containment of the Main COCs should also contain other chemicals, including benzene, toluene and other fuel related compounds, identified in the 2010 RI as chemicals exceeding screening levels.

The 2011 ROD also identified treatment standards for different end uses, which included ten of the 13 Main COCs and an additional eight or nine constituents, depending on end use. For the purposes of the PDI, the additional constituents will be referred to as “Key Treatment Constituents”. Based on the end use selected, extracted water will be treated for chemicals and constituents exceeding permit limits.

2.2.2 Distribution

The distribution of Main COCs and Key Treatment Constituents within and in the vicinity of the RDWA was evaluated as part of the data gaps analysis (PDI Work Plan, H+A, 2016). The following provides a summary of the current understanding of the general distribution of Main COCs in the RDWA. The distribution of COCs will be refined during the PDI to define the target zone for the NE and CE extraction wellfields and will be discussed in more detail in the PDI Report.

- Of the Main COC VOCs, PCE and TCE exceeded their respective MCLs over the largest area and greatest depth within the RDWA. Both of these compounds are common solvents used/handled by many sites within the RDWA and OU2.

The concentrations of these two compounds are generally greatest in the vicinity of source sites in shallow groundwater and have not been detected exceeding MCLs in monitoring wells deeper than 200 feet within the RDWA[1]. In addition, the concentration of these two compounds generally decreases toward the southern end of the CE Area; although there has been detection of relatively elevated concentrations of these compounds to the south of the RDWA, indicating the presence of source areas in the LE to the south of the CE Area.

- Freon 11 and Freon 113 were detected at lower concentrations and within the overall extent of areas of PCE and TCE detections. Freon 11 and Freon 113 were known to be used by businesses in OU2 and the types of businesses known to operate currently and historically in OU2 were the types of businesses that frequently utilized Freons. Freons are ubiquitous compounds, and Freon 11 and Freon 113 uses included dry cleaning, cold cleaning electrical parts, vapor phase cleaning, photographic film and magnetic tape cleaning, use in refrigerants, use in blowing agents, use in oil field activities, use in fire extinguishing, use in propellants, and use in oil field activities. Freon was also commonly found in both automotive and industrial waste oils.
- The remaining Main COC VOCs are generally within the overall extent of PCE and TCE.
- 1,4-Dioxane has been detected exceeding the NL over an area and depth similar to PCE and TCE, although at generally lower concentrations. This compound is often associated with the common solvent 1,1,1-trichloroethane, which has been used/handled by many sites within the RDWA. 1,4-Dioxane has not been analyzed in as many groundwater sample locations as VOCs; however, the concentration of 1,4-dioxane is generally greatest in the vicinity of source sites in shallow groundwater and has not been detected exceeding the NL in monitoring wells deeper than 200 feet within the RDWA[2].

[1] Note that the majority of the OU2 monitoring wells are not deeper than 200 feet below ground surface. Of the 28 well locations currently in the Work Area monitoring network, only wells MW25D (209 feet below ground surface), MW26D (205 feet below ground surface), and Hawkins (252, 296, 388, and 490 feet below ground surface) are screened deeper than 200 feet below ground surface.
[2] See footnote 1 above.

- Hexavalent chromium has been detected exceeding the MCL over a relatively wide area of the RDWA, although it does not appear to be as extensive as PCE and TCE or 1,4-dioxane. Hexavalent chromium has not been analyzed in as many groundwater sample locations as VOCs; however, the concentration of hexavalent chromium is generally greatest in the vicinity of source sites in shallow groundwater and has not been detected exceeding the MCL in monitoring wells deeper than 200 feet within the RDWA[3].

2.3 Activities Covered by the QAPP

This QAPP applies to the activities to be performed for the Work Area, consisting of the RDWA and the LE Area, within OU2 during the design of the NE/CE Area remedy. The main components of the NE/CE Area Work are extraction wellfields in the NE Area (in the vicinity of Sorensen Avenue) and the CE Area (in the vicinity of Telegraph Road); one or more treatment systems that will be determined by selected water end use; an end use of treated groundwater; associated conveyance pipelines; and Institutional Controls (ICs). Reinjection (shallow and/or deep), basin recharge, and reclamation will be evaluated during RD as potential end uses of the treated groundwater unless the SWDs and EPA mutually agree that it is no longer appropriate to evaluate one of the contemplated end uses after considering the cost-effectiveness and implementability of the end use.

Currently planned investigations and monitoring, as specified in the 2016 CD, include the PDI, the LEI, and Work Area groundwater monitoring. The PDI Work Plan (H+A, 2016) includes installation of new wells and sampling of groundwater in the NE/CE Area to refine the parameters needed for RD. Analytes for samples collected in the PDI will include the Main COCs and may include a number of additional analytes required to assess the various end uses of treated groundwater. The LEI Work Plan (Geosyntec, 2016a) includes installation of new wells in the LE Area. Analytes for samples collected in the LEI will include the Main COCs. The WAMP includes monitoring of the existing OU2 monitoring well network, as well as new wells installed in the PDI and LEI after those investigations are complete. Analytes for samples collected in routine groundwater monitoring will include the Main COCs.

[3] See footnote 1 on previous page.

2.4 Handling of Investigation-Derived Waste

The SWDs understand OU2 to be the type of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site where it is not possible, with any reasonable certainty, to know the source of contaminants in specific waste streams associated with individual OU2 remedial activities. The SWDs have therefore concluded that the IDW generated by the OU2 remedial activities will not be listed waste under the Resource Conservation and Recovery Act (RCRA), as documented in an August 8, 2016 memo to DTSC.

IDW generated from activities covered under this QAPP will be containerized, properly labeled, and temporarily stored at an appropriate location to be determined within the Work Area. Samples of IDW will be collected for waste profiling and sent to a California-certified laboratory for analysis in accordance with California Code of Regulations, Title 22, Section 66261.24. Following waste profiling, the IDW will be transported by a licensed waste hauler for disposal at an appropriately permitted solid or hazardous waste facility in accordance with Federal and State requirements, including valid EPA CERCLA Off-Site Rule approval (40 CFR 300.440). IDW will be stored for no more than 60 days during characterization and consolidation.

3. PROJECT ORGANIZATION

EPA, DTSC, and the SWDs will each designate a Project Coordinator who is responsible for overall coordination of work under their respective authority.

3.1 EPA

In accordance with the 2016 CD, EPA shall designate and notify the SWDs of its Project Coordinator and Alternate Project Coordinator. EPA may designate other representatives, which may include its employees, contractors and/or consultants, to oversee the Work. EPA's Project Coordinator/Alternate Project Coordinator will have the same authority as a remedial project manager and/or an on-scene coordinator, as described in the National Contingency Plan. This includes the authority to halt or modify the Work, and/or to conduct or direct any necessary response action in response to his or her determination that conditions at the Work Area constitute an emergency or may present an immediate threat to public health or welfare or the environment due to a release or threatened release of Waste Material.

3.2 DTSC

In accordance with the 2016 CD, DTSC shall designate and notify EPA and the SWDs of its Project Coordinator and Alternate Project Coordinator. DTSC may designate other representatives, including its employees, contractors and/or consultants to oversee the Work. For any in-person meetings and inspections in which EPA's Project Coordinator participates, DTSC's Project Coordinator also may participate. SWDs shall notify DTSC reasonably in advance of any such in-person meetings or inspections.

3.3 SWD Project Team

The SWD project team organization is shown in Figure 1 and described below.

3.3.1 Project Coordinator

The SWDs' Project Coordinator is the individual who represents the SWDs and is responsible for the overall coordination of the Work. In accordance with the 2016 CD, this SWD Project Coordinator must have sufficient technical expertise to conduct the Work and may not be an attorney representing any SWDs in this matter and may not act as the Supervising Contractor. SWDs' Project Coordinator may assign other

representatives, including other contractors, to assist in coordinating the Work. It is anticipated that Jack Keener of de maximis, inc. will be the SWD's Project Coordinator.

3.3.2 Supervising Contractor

SWDs must designate a Supervising Contractor by the due date of the Preliminary (30%) RD Report, as defined in the SOW. SWDs' proposed Supervising Contractor must have a quality assurance system that complies with ANSI/ASQC E4-2004, Quality Systems for Environmental Data and Technology Programs: Requirements with Guidance for Use (American National Standard).

3.3.3 Quality Assurance Manager

The primary responsibility for project quality rests with the Project Coordinator, while the Supervising Contractor and QA Manager provide independent QC. The Supervising Contractor and QA Manager (or their designees) will review project planning documents, data evaluation, and deliverables. If review of documents identifies QA problems or deficiencies requiring special action, the Project Coordinator, Supervising Contractor, and QA Manager will identify the appropriate corrective action for the field sampling personnel or the laboratory. As shown in Figure 1, the QA Manager is independent of the analytical laboratory and sample collection teams and reports directly to the Project Coordinator.

3.3.4 Health and Safety Coordinator

The project field personnel will implement the project in accordance with this QAPP, the Field Sampling Procedures, and the project Health and Safety Plan (HASP). The project health and safety coordinator confirms that field personnel are properly trained and prepared for field procedures as described in the HASP.

3.3.5 Special Training Requirements

The field personnel working on the Site will be trained in health and safety (CFR 1910.120) and will follow requirements specified in the HASP. The HASP describes the specialized training required for personnel on this project, and how it is to be documented and tracked.

3.4 Analytical Laboratory

Eurofins Calscience Inc. (Calscience) will perform chemical analyses of the environmental samples collected during monitoring activities. Calscience is certified through the National Environmental Laboratory Accreditation Program (NELAP), and the California Department of Health Services' Environmental Laboratory Accreditation Program (ELAP).

The NELAP meets the Quality System requirements of the EPA, complying with ANSI/ASQC-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Program*, (American National Standard, 1995), and *EPA Requirements for Quality Management Plans (QA/R-2)*, EPA/240/B-01/002, (EPA, 2006b). The certifications of the laboratory are included in Appendix A.

In accordance with the SOW (Section 7.7 (d) 2, 4), Calscience will perform all analyses using EPA-accepted methods and will participate in a QA/QC program acceptable by EPA. The Calscience Quality Assurance Manual is presented in Appendix A.

4. QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Presented below is a brief discussion of the DQOs and Data Quality Indicators (DQIs) for the project, along with the methods used to evaluate data quality.

4.1 Data Quality Objectives

DQOs are qualitative and quantitative statements that clarify the project objectives, specify the most appropriate type of data for the project decisions, determine the most appropriate conditions from which to collect data, and specify tolerable limits on decision errors. DQOs are based on the end uses of the data and are determined through a seven-step process as described in QA/G-4 (EPA, 2006). In addition to the project objectives, the DQOs specify data collection boundaries and limitations, the most appropriate type of data to collect, and the level of decision error that will be acceptable.

The DQO process is a series of planning steps based on scientific methods that are designed to ensure that the type, quantity, and quality of environmental data used for decision-making are appropriate for the intended application. The DQO process, as defined by EPA, consists of seven steps that are designed to provide a systematic approach to resolving issues that pertain to site investigation and remediation (EPA, 2006a). The DQOs for this project were developed from discussions with the stakeholders, technical experts, quality assurance staff, laboratory representatives, and project management, as well as from all available historical data and information.

The DQOs were developed following guidance provided by EPA, *Guidance on Systematic Planning Using the Data Quality Objectives Process,* EPA QA/G-4 (EPA, 2006a). Performing the DQO process is generally one of the first prerequisite steps to data collection. It is a planning process from which qualitative and quantitative results are derived in relation to a particular data collection event (or group of events). The steps to the DQO process are as follows:

- Step 1 – State the Problem
- Step 2 – Identify the Goal of the Study
- Step 3 – Identify Information Inputs
- Step 4 – Define the Boundaries of the Study

- Step 5 – Develop the Analytic Approach
- Step 6 – Specify Performance or Acceptance Criteria
- Step 7 – Develop the Plan for Obtaining Data

DQOs were developed and described in detail in the respective work plans:

- LEIWP (Geosyntec, 2016a);
- PDIWP (H+A, 2016); and
- WAMP (Geosyntec, 2016b).

Summaries of the DQOs are presented in Tables 1a through 1c.

The DQO processes have been and will be undertaken in an interactive and iterative manner whereby the elements of the DQO steps are continually reviewed and applied during execution of the project. The DQO steps for each problem statement are given in Tables 1a through 1c. In order to fulfill the criteria for data collection during the DQO process, the following field activities are anticipated:

- Lithologic logging, including field observations and geophysical logging;
- Water level measurements; and
- Groundwater sampling and analysis.

4.2 Data Quality Indicators (PARCCS Parameters)

The QA program addresses both field and laboratory activities. QA objectives are formally measured through the computation of performance measures known as DQIs, which are in turn compared to pre-defined Measurement Quality Objectives (MQOs) specific to the project objectives. The DQIs for measurement data are expressed in terms of precision, accuracy, representativeness, completeness, comparability, and sensitivity (PARCCS). Evaluation of DQIs provides the mechanism for ongoing control and evaluation of data quality throughout the project and ultimately will be used to define the data quality achieved for the various measurement parameters. The field QA/QC program will be accomplished through the collection of field duplicates, equipment blanks, field blanks, filter blanks, and trip blanks. The analytical QA/QC program will be assessed through the internal laboratory QC performed, including

method blanks, laboratory control sample (LCS) recoveries, surrogate recoveries, and matrix spike/matrix spike duplicate (MS/MSD) recoveries. The following sections describe the DQIs in greater detail, with a discussion of the associated MQOs.

4.2.1 Precision

Precision is a measure of the mutual agreement between individual measurements of the same property, usually under prescribed similar or identical conditions. Precision is estimated by the standard deviation around the mean or relative percent difference (RPD) between two samples. The RPD between duplicate sample results is calculated using the equation below:

$$RPD = \left| \frac{D1 - D2}{\left(\frac{D1 + D2}{2}\right)} \right| \times 100\%$$

Where: D1 = first sample value
D2 = second sample value (duplicate)

If calculated from three or more replicates, the relative standard deviation (RSD) shall be used rather than the RPD:

$$RSD = \left(\frac{s}{y}\right) \times 100\%$$

Where: RSD = relative standard deviation
s = standard deviation
y = mean of replicate analyses

Standard deviation, s, is defined as follows:

$$s = \sqrt{\sum_{i=1}^{n} \frac{(y_i - y)^2}{n - 1}}$$

Where: s = standard deviation
y_i = measured value of the i^{th} replicate

y = mean of replicate analyses
n = number of replicates

The RPD/RSD project goal is 30% for aqueous samples and 50% for soil samples.

The precision of a reported result is a function of sample homogeneity, inherent field related variability, shipping variability, and laboratory analytical variability. Precision will be determined through the collection of field duplicates and the analysis of matrix spike/matrix spike duplicate (MS/MSD) and laboratory control sample/laboratory control sample duplicate (LCS/LCSD) pairs for the work performed at the Site. The overall precision of measurement data is a mixture of sampling and analytical factors. Analytical precision is much easier to control and quantify than sampling precision; there are more historical data related to individual method performance, and the "universe" is not limited to the samples received in the laboratory. In contrast, sampling precision is unique to the project. Sampling precision will be measured through the laboratory analysis of field duplicate samples. Laboratory precision will be measured through the analysis of MS/MSD and LCS/LCSD samples. Field duplicates should be collected at a frequency of one per day of sampling to assess sampling method variation.

4.2.2 Accuracy and Bias

Accuracy refers to the degree of difference between measured or calculated values and the true value. The closer the numerical value of the measurement comes to the true value, or actual concentration, the more accurate the measurement. The converse of accuracy is bias, in which a systematic mechanism tends to consistently introduce errors in one direction or the other. Bias in environmental sampling can occur in one of three ways; these mechanisms and their associated diagnostic and management methods are as follows:

- High bias, which can stem from cross-contamination of sampling, packaging, or analytical equipment and materials. Cross-contamination is monitored through blank samples, such as equipment blanks, field blanks, trip blanks, filter blanks, and method blanks. These samples assess the potential for cross-contamination from, respectively, sampling equipment, ambient conditions, packaging and shipping procedures, field filters, and laboratory equipment. Data validation

protocols described in Section 5 present a structured approach for data qualification based on blank samples.

- Low bias, which can stem from the dispersion and degradation of target analytes; an example is the volatilization of chlorinated solvents during field sampling. The effects of these mechanisms are difficult to quantify. Sampling accuracy can be maximized, however, by the adoption and adherence to a strict field QA program. Specifically, sampling procedures will be performed following standard protocols described in the FSPs (Geosyntec, 2016; H+A, 2016); for example, eliminating headspace in sampling vials for VOCs will reduce the potential for dispersion of VOCs during sampling. Through regular review of field procedures, deficiencies will be documented and corrected in a timely manner.
- High or low bias, due to poor recoveries, poor calibration, or other system control problems. The effects of these mechanisms on analytical accuracy may be expressed as the percent recovery of an analyte that has been added to the environmental sample at a known concentration before analysis. Analytical accuracy in the laboratory will be determined through the analysis of LCSs and MS/MSDs. As with blank samples, data validation protocols provide a structured formula for data qualification based on erroneously high or low analyte recoveries.

Accuracy is presented as percent recovery (%R) and is calculated using the equation below:

$$R = \frac{(A - X)}{T} \times 100\%$$

Where: R = percent recovery
A = measured value of the analyte after spike is added
X = measured value of analyte concentration in sample before the spike is added
T = value of the spike

Accuracy goals for the project are listed by method in Tables 3a and 3b.

4.2.3 Representativeness

Representativeness is the degree to which data accurately and precisely represent the true value of a characteristic of a population, a process condition, parameter variations at a sampling point, or an environmental condition. The representativeness of reported results depends upon a number of considerations, including but not limited to, proper monitoring design, selection of appropriate field methodology, proper sample preparation, preservation and handling, selection and execution of appropriate analytical methodology, and proper sample identification and reporting of results. It also extends to sample location, number of samples, and the actual material collected, so that the results are always representative of the population to be described.

Documentation requirements performed per the specification of this QAPP establish that the protocols have been followed and sample identification and integrity are assured. If data appear to deviate from an anticipated trend (from comparison of the data to historical data), further investigations into the collection methodology and QA/QC procedures will be initiated to resolve the questionable data.

4.2.4 Completeness

Completeness (C) is expressed as the percentage of all measurements made whose results are judged to be valid. Valid data are defined as all data that meet the quality assurance criteria for the project and are not rejected. The following formula is used to estimate completeness:

$$C = \frac{V}{T} \times 100\%$$

Where: C = percent completeness
V = number of measurements judged valid
T = total number of measurements

Field and analytical data may be specified at different levels of completeness. The completeness criteria should be defined to be consistent with the project data quality objectives. The QA objective for completeness for all parameters will be 90%.

4.2.5 Comparability

Comparability is a characteristic that refers to the similarity of data from different sources. It is the confidence with which one data set can be compared to another. Comparability may be assessed in terms of sampling plans, analytical methods, QC, and data reporting. The comparability requirements for field measurement and sampling activities will be maintained by following protocols and procedures specified in this document.

4.2.6 Sensitivity

Sensitivity refers to the minimum magnitude at which analytical methods can resolve quantitative differences among sample concentrations. If the minimum magnitude for a particular analytical method is sufficiently below an action level or risk screening criterion, then the method sensitivity is deemed sufficient to fully evaluate the data set with respect to the desired reference values.

The method detection limit (MDL) is a theoretical limit determined through an MDL study, in which the concentration of a spiked solution is tested at least seven times. The standard deviation of the recovered concentrations is computed and multiplied by the Student's t-distribution value to arrive at the MDL. The method reporting limit (RL) is often based on either the lowest point on the calibration curve or a low point on the curve and is quantifiable. In practice, to allow for matrix interference variability in instrument control, a RL of 2.5 to 5 times the MDL is typically selected.

4.3 Analytical Levels

Field and analytical data can be used for a number of purposes ranging from qualitative field and screening data to quantifiable enforcement level data. To ensure that the data will be usable for their intended purpose, analytical reporting levels have been defined for the data package which consider data uses, types of technology, and documentation. The levels range from I – IV, and a description is given in Table 4.

For the OU2 project, 90% of all samples submitted for laboratory analyses will be reported according to Level II data quality requirements, with 10% of all samples reported according to Level IV data quality requirements. In order to ensure that the data generated for this project are of known quality, the laboratory will be required to submit a data package that emulates EPA's Contract Laboratory Program Statement of

Work (CLP-SOW) requirements for Organic and Inorganic Superfund Methods (EPA, 2015b and 2015c). It is not anticipated that the other Levels will be required for this project.

A Level II deliverable will include the following:

- Cover sheet signed by the laboratory manager or their designee;
- Case narrative;
- Sample results;
- Laboratory QC results;
- Copy of the chain of custody received with the samples; and
- Copy of laboratory sample receipt form.

A Level IV or CLP-like data package will include the following:

- All of the data included in a Level II deliverable; and
- All raw data to check for technical issues as compared to the analytical method requirements which includes:
    - Chromatograms/instrument printouts for samples and standards,
    - Calibration results for each test,
    - Calibration check standards for each test,
    - Sample preparation work sheets,
    - Chemical standard information,
    - Instrument run logs,
    - Internal standard data,
    - Retention time window calculations, and
    - Instrument tune information.

4.4 Data Uses Summary

After each data collection activity and subsequent data validation, an assessment of the data usability will be made. This assessment will compare the results with DQOs and will be used to guide future sampling and analysis activities.

5. SAMPLING PROCEDURES

The objectives of the sampling procedures and field measurements are to obtain samples and measurements that accurately and precisely represent the environmental site being investigated. Proper sampling equipment and decontamination procedures must be used in order to eliminate trace levels of contaminants from external sources.

5.1 Notifications

EPA will be given at least 14 days' notice prior to any sample collection activity in accordance with the SOW (Section 7.7 (d) 5). The 14-day notification will allow EPA to prepare to take additional samples that it deems necessary in accordance with the SOW (Section 7.7 (d) 7).

5.2 Equipment Decontamination

If used, non-dedicated sampling equipment will be decontaminated before and after samples are collected. Decontamination will consist of (in the following order): detergent (e.g., Alconox) and water wash, potable water rinse, and distilled water rinse. Protocols for decontamination of non-dedicated equipment are included in the Field SOPs for water level measurements, water quality parameter measurements, and groundwater sample collection (Geosyntec, 2016a; H+A, 2016). Equipment rinsate blanks will be used to assess proper decontamination of non-dedicated sampling equipment.

5.3 Supplies

Supplies and materials used either in the field or the laboratory shall be standard industry material. The supplies and materials shall be inspected prior to use, be in good working condition, and within the expiration date requirements specified by the manufacturer.

5.4 Sample Handling

Groundwater and soil samples will be preserved with chemicals appropriate for the analyses and stored on ice immediately after sampling (see detailed handling protocols in Tables 5a through 5d). Nitrile gloves will be worn when handling groundwater samples or sampling equipment. Breakable or otherwise fragile sample containers will

be wrapped in plastic bubble-wrap to prevent damage during shipment. Samples will be delivered to the laboratory by courier on the same day of collection or the following day.

5.5 Field Quality Control Samples

Field QC samples are used to evaluate conditions resulting from field activities and are intended to accomplish two primary goals, assessment of field contamination and assessment of sampling variability. The former identifies substances introduced in the field due to sampling equipment or sampling practices and is assessed using blanks of different types. The latter includes variability due to sampling technique and instrument performance as well as variability possibly caused by the heterogeneity of the matrix being sampled and is assessed using replicate sample collection. A summary of the field QC sample frequency is provided in Table 6. The following sections cover field QC in accordance with EPA Region IX guidelines (EPA, 2004).

5.5.1 Equipment (Rinsate) Blanks

Equipment rinsate blanks will be collected to evaluate field sampling and decontamination procedures of non-dedicated sampling equipment. Equipment rinsate blanks will be collected by pouring reagent-grade deionized water provided by the laboratory over the decontaminated sampling equipment. One equipment rinsate blank will be collected per matrix each day that sampling equipment is decontaminated in the field or for every 10 samples collected, whichever is more frequent. Equipment rinsate blanks will be obtained by passing water through or over the decontaminated sampling devices used that day. The rinsate blanks that are collected will be analyzed for the same analytes as the samples collected with the equipment.

The equipment rinsate blanks will be preserved, packaged, and sealed in the manner described for the environmental samples (Tables 5a through 5d). A separate sample number and station number will be assigned to each sample, and it will be submitted blind to the laboratory.

5.5.2 Field Blanks

Field blank samples will be obtained by filling a clean sampling container with reagent-grade deionized water provided by the laboratory. The sample will then be submitted for analysis. Field blank samples will be collected and analyzed during the project to

assess potential background contamination or errors in the sampling process. Field blanks will be collected daily when dedicated equipment is used and equipment (rinsate) blanks are not collected.

5.5.3 Trip Blanks

Trip blanks will be analyzed to evaluate if the shipping and handling procedures are introducing contaminants into the samples, and if cross contamination in the form of VOC migration has occurred between the collected samples. Trip blanks, consisting of reagent-grade deionized water, will be transported from the analytical laboratory to the sampling site, and then returned to the laboratory along with the field samples without having been opened in the field. A minimum of one trip blank will be submitted to the laboratory for analysis in each cooler containing samples for analysis. A separate sample number and station number will be assigned to each trip sample. If no VOCs are to be analyzed, a trip blank is not needed. Trip blanks are used in association with aqueous field samples.

5.6 Field Duplicates

The purpose of a field duplicate sample is to evaluate the precision of both sampling techniques and laboratory testing. A duplicate sample shall be collected, labeled, packaged, and stored in the same manner as any other sample. The duplicate groundwater sample will be collected serially from the source. Analysis will be the same as those required for the parent sample. A duplicate sample set consists of a complete set of samples of the appropriate volume and in the appropriate containers which is the same as a standard sample set.

Field duplicate samples will be collected one for every 10 samples (10%). Each field duplicate will be assigned its own sample identification number so that it will be blind to the laboratory. A field duplicate sample is treated independently of its counterpart in order to assess laboratory performance through comparison of the results.

In accordance with the SOW (Section 7.7 (d) 8), EPA may collect and provide duplicate samples to SWDs in connection with EPA's oversight sampling.

5.7 Split Samples

In accordance with the SOW (Section 7.7 (d) 6), split samples will be collected upon requests from EPA for analysis by a separate laboratory designated and contracted by EPA. In order to produce a split sample, twice the volume of sample will be collected and then split between the requisite sample containers needed to conduct the analyses required for the specific sampling location. If split sampling occurs, documentation on the field logs and field notebook will include the agency collecting the sample and which samples were collected for which parameters.

If split samples are requested, sampling locations, sampling method, and sampling analyses will be discussed with the EPA before the field activities. EPA may also collect and provide split samples to SWDs in connection with EPA's oversight sampling.

6. DOCUMENTS AND RECORDS

6.1 Project Files

The project files will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. The Project Coordinator is the custodian of the project files and will maintain the contents of the project files for the duration of the work, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area and under custody of the Project Coordinator.

The project files will include at a minimum:

- Field logs;
- Field data (including electronic files and data deliverables);
- Photographs;
- Drawings;
- Sample collection logs;
- Laboratory data deliverables;
- Data validation reports (DVRs);
- Data assessment reports;
- Progress reports, QA reports, interim project reports, etc.; and
- All custody documentation (chain of custody forms, airbills, etc.).

Electronic versions of correspondence, reports, drawings, and calculations will be stored in the project-specific network file. The original EDDs received from the laboratories, and the project database, will also be stored on the network, which is backed up and periodically archived off-site.

Project records will be retained per Section XX of the CD (EPA, 2016). Records associated with the Work will be retained with all the project records for 5 years after EPA's Certification of Work Completion as described in the CD. EPA and DTSC will

be notified in writing 90 days prior to destruction of any records, and if requested, the SWDs will deliver these records to EPA or DTSC.

6.2 Field Records

Sample identification, sample collection, and field measurement records will be maintained in field records, including, at a minimum, a Daily Log. Depending on the activity, field records will be recorded on additional forms such as boring logs, water level measurements, and well sampling logs. Field observations not recorded on an activity-specific form will be recorded on the Daily Log.

At a minimum, the following information will be recorded during the collection of each sample:

- Sample location and description;
- Site or sampling area sketch showing sample location and measured distances;
- Sampler's name(s);
- Date and time of sample collection;
- Designation of sample as composite or grab;
- Type of sample (soil, sediment or water);
- Type of sampling equipment used;
- Field instrument readings and calibration;
- Field observations and details related to analysis or integrity of samples (e.g., weather conditions, noticeable odors, colors, etc.);
- Preliminary sample descriptions (e.g., for soils: sandy silt, dry; for water: clear water with strong odor);
- Sample preservation;
- Lot numbers of the sample containers, sample identification numbers and any explanatory codes, and chain-of-custody form numbers; and
- Shipping arrangements (overnight air bill number).

In addition to the sampling information, the following specific information will also be recorded in the Daily Log for each day of sampling:

- Team members and their responsibilities;
- Time of arrival/entry on site and time of site departure;
- Other personnel on site;
- Summary of any meetings or discussions with tribal, contractor, or federal agency personnel;
- Deviations from sampling plans, site safety plans, SOPs and QAPP procedures;
- Changes in personnel and responsibilities with reasons for the changes; and
- Calibration readings for any equipment used and equipment model and serial number.

6.3 Sample Labels

Each collected sample will have a completed sample label securely attached to it. All field QC samples will be shipped "blind" (not identified as a QC sample) to the laboratory, but will be assigned a unique identification code in order to facilitate identification of the laboratory results. Sample collection labels will include the sample ID, the location of the sampling site or site code, the type of sample, the sample matrix, the time of sampling, sample preservation, the requested sample analysis, and the initials of the sampler. Labels will be pre-printed to the extent possible to ensure that the required information is provided on each label. The field personnel who physically collects the sample is the sampler and will complete and initial the sample label.

6.4 Chain-of-Custody Requirements

The sample custody procedure documents the identity of the sample and its handling from its first existence as a sample until information derived from it is introduced as evidence. Custody records trace a sample from its collection through all transfers of custody until it is transferred to an analytical laboratory. Internal laboratory records then document the custody of the sample through its final stages of documentation.

The *National Enforcement Investigations Center Policies and Procedures Manual, EPA- 330/9-97-002R* (EPA, 2005b) provides chain-of-custody and document control

procedures and all sample identification records and custody records will be used to satisfy the requirements of the EPA. The following sections discuss the chain-of-custody and document control requirements specified in the above document that are appropriate to this project. If any deviations occur from these procedures, the appropriate personnel will be notified and deviations will be noted in the field forms.

A sample or other physical evidence is in custody if it is/was:

- in the field investigator's, transferee's, or lab technician's actual possession;
- in the field investigator's, transferee's, or lab technician's view, after being in his/her physical possession;
- in the field investigator's, transferee's, or lab technician's physical possession and then he/she secured it to prevent tampering; or
- placed in a designated secure area.

6.4.1 Field Custody Requirements

The field team will have a field sample custodian that is designated with the overall responsibility for sample custody and for field document control. The chain-of-custody will be maintained for samples collected in the field and transported or shipped to the laboratory for analysis. The custodian will ensure that the sampling teams have the appropriate identification and custody records, resolve custody problems in the field, and will handle the shipment of samples to the analytical laboratory. Each analytical laboratory will have an identified sample custodian. A sample chain-of-custody record sheet is provided in Appendix A.

6.4.2 Chain-of-Custody Record Sheets

Sample collection and sample custody procedures are designed so that field custody of samples is maintained and documented. These procedures provide identification and documentation of the sampling event and the sample chain-of-custody from sample collection through receipt of the sample by the subcontracted laboratory and ultimately sample disposal. When used in conjunction with the laboratory's custody procedures and the sample bottleware documentation, these data establish full legal custody and allow complete tracking of a sample from preparation and receipt of sample bottleware to sample collection, preservation, and shipping through laboratory receipt, sample

analysis and data validation. The chain-of-custody is defined as the sequence of persons who have the item in custody.

The field Chain-of-Custody Record is used to record the custody of all samples or other physical evidence collected and maintained. The Chain-of-Custody Record also serves as an initial sample logging mechanism for the analytical laboratories' sample custodian.

The following information must be supplied in the indicated spaces in detail to complete the field Chain-of-Custody Record:

- Project specific information, including the project number and project name.
- The signatures of all samplers and/or the sampling team leader in the designated signature block.
- The sampling station number, date, and time of sample collection, grab or composite sample designation, and sample preservation type must be included on each line (each line shall contain only those samples collected at a specific location).
- The sampling team leader's name should be recorded in the right or left margin of the Chain-of-Custody Record when samples collected by more than one sampling team are included on the same form.
- The total number of sample containers must be listed in the indicated space for each sample and the total number of individual containers must also be listed for each type of analysis under the indicated media or miscellaneous columns (note that it is impossible to have more than one media type per sample).
- The field investigator and subsequent transferee(s) must document the transfer of the samples listed on the Chain-of-Custody Record in the spaces provided at the bottom of the form (both the person relinquishing the samples and the person receiving them must sign the form; provide the date and time that this occurred in the proper space on the form; and usually, the last person receiving the samples or evidence should be a laboratory sample custodian).
- The remarks column at the bottom of the form is used to record air bill numbers or registered or certified mail serial numbers.

The Chain-of-Custody Record is a serialized document. Once the Record is completed, it becomes an accountable document and must be maintained in the project file. The suitability of any other form for chain-of-custody should be evaluated upon its inclusion of all of the above information in a legible format.

Laboratory personnel are responsible for sample custody within the laboratory in accordance with their laboratory QA manual (Appendix A).

6.4.3 Laboratory Custody Procedures

Each sample shipment will be inspected to assess the condition of the shipping container and the individual samples upon receipt at the laboratory. The enclosed chain-of-custody records will be cross-referenced with all of the samples in the shipment and these records will be signed by the sample custodian and placed in the project file. In the event of a discrepancy between the sample label numbers and custody record listings, the samples in question will not be analyzed until the discrepancy is resolved and the resolution documented.

6.5 Packaging and Sample Shipment

All samples collected during the field activities and shipped for laboratory analysis will be packed in accordance with Department of Transportation (DOT) regulations. Sample containers will be placed in re-sealable plastic bags with packing material designed to prevent breakage during shipment. Sample containers will be placed in sample coolers provided by the analytical laboratory. Wet ice will be placed in the sample coolers to maintain sample preservation requirements. The chain-of-custody record will also be placed in a re-sealable bag and then taped onto the lid of the sample cooler. All samples will be shipped to the laboratory or picked up from the site by the laboratory on the day of collection or the day after. The field sample custodian will notify the laboratory sample custodian of the sample delivery prior to the day the samples are to be delivered.

6.6 Corrections to Documentation

Waterproof ink will be used to record all original data recorded in field records, sample labels, chain-of-custody sheets, and receipts-for-sample forms. Record corrections are made by drawing a single line through the error, entering their initials and date of the correction, and entering the correct information. Errors shall not be obliterated or written over. If an error is identified after the fact, the person who originally made the

entry should correct any subsequent error discovered on an accountable document and then initial and date the corrections. The dates and time recorded are for the dates and times that the corrections were actually made to the documentation.

7. EQUIPMENT CALIBRATION AND MAINTENANCE PROCEDURES

7.1 Laboratory Calibration Procedures

All calibrations will be as defined per the standard EPA methodology applicable to project required analyses as summarized in Table 7.

7.2 Laboratory Maintenance procedures

The laboratories maintain instrument maintenance logs at all times. The logs, in general, contain a schedule of maintenance, as well as a complete history of past maintenance, both routine and non-routine.

The laboratory performs preventive maintenance according to the procedures described in the manufacturer's instrument manuals, including lubrication, source cleaning, detector cleaning, and frequency of such maintenance.

The laboratory also examines precision and accuracy data for trends and excursions beyond control limits to determine evidence of instrument malfunction.

The laboratory will perform maintenance when an instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decrease in sensitivity, or failure to meet one or another of the QC criteria.

The laboratory minimizes instrument downtime by keeping adequate supplies of all expendable items, where expendable means an expected lifetime of less than one year.

7.3 Field Calibration Procedures

All equipment used during field activities will be operated, maintained, calibrated, and standardized according to the manufacturer’s recommended procedures and by following procedures described in the FSPs (Geosyntec, 2016a; H+A, 2016). All maintenance and calibration operations will be documented in the field records. The field equipment shall have a protocol which contains the following, as appropriate:

- Standard operating procedures which describe:
    - Routine preventative maintenance procedures including possible spare parts to be available in the field;

- Calibration methods, frequency and description of calibration solutions;
- Standardization procedures; and
- Precision and accuracy assessment procedures.

Before use, all field equipment will be checked and calibrated to show that it is in good working order, in accordance with the Field SOPs (Geosyntec, 2016a; H+A, 2016). Measurement data for water quality parameters will be compared to historical data from the well, if existing data are available.

7.4 Field Preventative Maintenance

All field equipment will have preventative maintenance carried out in accordance with procedures and schedules specified by the manufacturer and presented in the FSPs (Geosyntec, 2016a; H+A, 2016). Generally, all field equipment probes will be thoroughly rinsed with distilled water prior to each use and will be stored according to the manufacturer's instructions. The field instrument preventative maintenance requirements are summarized in Table 8.

8. ANALYTICAL PROCEDURES

8.1 Analytical Method Requirements

The analytical laboratory that will analyze the samples collected during the PDI activities (H+A, 2016), LEI activities (Geosyntec, 2016a), and groundwater monitoring activities (Geosyntec, 2016b) will conduct the analytical work according to the methods specified in Tables 3a and 3b and in accordance with the SOW (Section 7.7 (d), 3). Analytical methods proposed for this project will allow for the detection of COCs and other analytes of interest at their respective MCLs or NLs, as listed in Tables 5a through 5d. Where needed to meet MCLs or minimum detection levels for the project, low-level drinking water methods have been provided in the tables as alternates to the standard SW-846 methods.

8.2 Laboratory QA/QC Requirements

Applicable method QC requirements highlighted in this QAPP, as well as the requirements present in the referenced methods, will be followed by the project laboratory in accordance with the SOW (Section 7.7 (d), 2, 4). The laboratory performing the analyses will submit documentation to show that all of the QC criteria are satisfied for the analyses. Calscience has provided their QA Manual, which describes the corrective actions and outlines the QA responsibilities within the laboratory and is provided in Appendix A. The laboratory's certifications are also included in Appendix A.

Tables 3a, 3b, and 7 present a summary of laboratory QC requirements, which includes control limits established for laboratory QC samples analyzed with the project samples. All method-specific QC measures, such as external and internal standard calibration procedures, instrument performance verifications, and method standard quantitation must be performed. Laboratory-specific SOPs are included in Appendix B.

The general practices required of the laboratory are given below.

8.2.1 Purity of Standards, Solvents, and Reagents

Laboratory reagents must be of reagent-grade or higher quality whenever obtainable. Organic solvents will be pesticide grade or equivalent. Also, reference standard solutions will be traceable to certified reference materials as described in Appendix A.

Each new lot of reagent-grade chemicals will be tested for quality of performance, and laboratory records will be kept to document the results.

8.2.2 Analytical QC Samples

8.2.2.1 Laboratory Reagent-Grade Water

Laboratory reagent-grade water is prepared by a special deionized water system augmented by individual filter cartridges and polishers located at each outlet point. Laboratory reagent-grade water will be tested to demonstrate that it is free of contaminants at levels below half the RLs for the project analytes of concern.

8.2.2.2 Method Blank/Reagent Blank/Calibration Blank

A laboratory method blank must be analyzed along with all aqueous and non-aqueous samples submitted for analyses. The method blank is processed through all materials, reagents, labware, and procedures used for sample preparation and analysis. The frequency for method blank analysis is a minimum of 1 per 20 samples or per extraction and/or analytical batch (depending on the method requirements), whichever is more frequent. An extraction/analytical batch is defined as a maximum of 20 samples that are extracted or analyzed together with the same method sequence. Sample preparation must employ the same lot of reagents with the manipulations common to each sample within the same 24-hour time period. Samples in each batch must be of similar composition or matrix.

8.2.2.3 Calibration Standards

The calibration standards are prepared in the laboratory by dissolving a known amount of analyte in an appropriate matrix or through the use of purchased commercial standards. The concentration is either provided by the vendor or calculated from the known quantity and is the true value of the standard. All calibration standards must be traceable to National Institute of Standards and Technology (NIST) certified reference materials or certified check standards. The results from these standards are used to generate a curve which can be used to quantify the compound in the environmental sample.

Table 7 shows the calibration information for the methods that will be used in this study.

8.2.2.4 Initial Calibration Verification

The initial calibration verification (ICV) is performed using a second source reference standard acquired from an EPA Standards Repository or the National Bureau of Standards (NBS) as described in Appendix A. The ICV is obtained from a separate source other than the standard used to generate the calibration curve. It is analyzed as is or diluted according to instructions provided with the reference material to provide independent verification of instrument calibration.

Initial Calibration Verification will be analyzed at a minimum of each time a new calibration curve is established, or at a frequency specified in the referenced protocols.

8.2.2.5 Control Samples

The LCS is a QC sample that is carried along with the samples through the entire extraction/analysis protocol. Solid and liquid matrix control samples are extracted and analyzed as applicable. The frequency for the LCS is 1 per 20 samples or as stated in the referenced protocol.

8.2.2.6 Matrix Spikes

A sample matrix spike is prepared by adding a known amount of pure analyte to the environmental sample before extraction. A post-extraction spike is prepared by adding a known amount of analyte to a known amount of sample extract. The purpose of the spike is to observe the effect of background and interferences on the actual sample analyte that has a similar effect on the spike. The calculated percent recovery of the matrix spike is considered to be a measure of the accuracy of the analytical method, which includes the sample preparation and analysis. The calculated percent recovery of the post-extraction spike is considered to be a measure of the accuracy of the sample analysis procedure only.

The limits of tolerance of the acceptable percent recoveries are established in the referenced methods and are summarized in Tables 3a and 3b. Matrix spikes will be analyzed at a minimum frequency of 1 per 20 samples of similar matrix or analytical batch.

Matrix spike duplicate (MSD) samples are required at a specified frequency of 1 per 20 samples. The MSD is prepared from a second aliquot of the sample that was analyzed as

the matrix spike. The RPD value between the matrix spike and the matrix spike duplicate (see calculation in Section 4.2.1) must be reported.

8.2.2.7 Surrogate Spikes

Surrogate compounds are similar in chemical composition to the target analytes and are spiked into samples, the method blank, laboratory control sample, matrix spike, and the matrix spike duplicate, prior to sample extraction/preparation as appropriate to each analytical method. The surrogate compounds selected are usually not found in environmental samples. The percent recovery of the surrogate is documented for each sample, indicating that all samples have gone through the analytical process with acceptable uniformity. The control limits for surrogate recovery vary from analysis to analysis. Corrective action must be taken on any surrogate recovery outside the control limit.

8.2.2.8 Laboratory Duplicate Sample

Aliquots of the same sample are made in the laboratory and each aliquot is treated exactly the same throughout the analytical method. The RPD between the duplicate values, as calculated in Section 4.2.1, is taken as a measure of the precision (reproducibility) of the analytical method for the sample matrix.

The laboratory duplicate is a measure of the laboratory sampling and analysis procedures and of the sample matrix homogeneity. Laboratory duplicates will be analyzed at a minimum frequency of 1 per 20 samples or per analytical batch.

9. DATA REDUCTION, VALIDATION, AND REPORTING

Reduction of laboratory measurement and laboratory reporting of analytical parameters will be in accordance with the procedures specified for each analytical method. Appendix C shows the electronic data deliverable (EDD) requirements that must be provided as the laboratory sample deliverable. Table 9 presents the hardcopy data deliverable requirements. Tables 5a through 5d show project reporting limits for each analyte, as well as the holding times, container selection, and preservation requirements. All method deviations and reporting or calculation variances will be fully documented by the project laboratory. Technical personnel that are qualified in data validation procedures will be responsible for data validation assessment.

9.1 Data Validation and Assessment: General Approach

Data quality and usability are dependent on many factors, which include sampling methods, sample preparation, analytical methods, quality control, and documentation. Subcontractors such as laboratories must be advised of all applicable documentation and procedural requirements. Once the data are collected, satisfaction of all validation criteria will be documented as listed below. Chemical data must meet criteria of: (1) quantitative statistical significance; (2) custody and document control; and (3) sample representativeness. Physical data include: (1) sampling location, time and personnel; (2) documentation; and (3) methodologies. Data validation and assessment of analytical data will be performed by the QA manager or their designee, who is not affiliated with the analytical laboratory, sample collection, or analytical data reduction. Other forms of data, as listed in Section 9.1.1 will be assessed by technical personnel, under the supervision of the QA manager.

9.1.1 Data Validation Procedures

The data types that will be used for the LEI, PDI, and WAMP activities include:

- Historical and new groundwater quality data from existing monitoring and production wells;
- Groundwater quality data collected from the monitoring well network; and
- Water level, well head elevation, and screen interval depth, or elevation data for all wells from which water quality data are used.

9.1.1.1 Data Validation of Laboratory Data

Data validation will be performed on all laboratory data generated during each activity sampling processes. Data validation can be defined as a data review process which provides information on the analytical limitations of data based on QC criteria. It provides specific usability statements for the data and aids in establishing whether data meet the general requirements set forth in the CLP-SOW and per the requirements of the analytical methodologies employed. Data validation will be performed according to the guidelines of the EPA *CLP National Functional Guidelines for Superfund Organic Methods Data Review* (EPA, 2014a) and EPA *CLP National Functional Guidelines for Inorganic Data Review* (EPA, 2014b), as well as *Region IX validation guidelines, R9QA/006.1* (Draft Dec., 2001a). During validation the following qualifiers will be applied to the data as applicable:

Data Qualifier	Definition
U	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
NJ	The analyte has been "tentatively identified" or "presumptively" as present and the associated numerical value is the estimated concentration in the sample.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting QC criteria. The analyte may or may not be present in the sample.

Approximately 10% of the data will be received from the laboratory as Level IV data packages and will undergo Stage 4 data validation (as defined in *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*; EPA, 2009). The QC elements that are necessary to complete a Stage 4 data validation include a case narrative, signed by the laboratory manager or his designee; sample results; all supporting raw data for the sample results; the quality assurance sample results that are associated with the samples including calibration data; continuing calibration data; sample extraction logs; analytical run sequences; surrogate data; internal standard data; retention time windows; instrument tuning data; and a copy of the chain-of-custody forms that were received with the samples. A Stage 4 data validation consists of checking the reported results against the supporting data; recalculation of the reported results from the raw data; verification (calculation) of the appropriateness and

acceptance of QC results associated with the data; checking technical holding times; and a completeness audit to ensure that all sample results are present as requested by the chain-of-custody and that QC results are within specified method criteria.

The remainder of the data will be received from the laboratory as Level II data packages and undergo Stage 2A data validation (EPA, 2009). The QC elements that are necessary to complete Stage 2A data validation include a case narrative, signed by the laboratory manager or his designee; sample results; the quality assurance sample results that are associated with the samples; and a copy of the chain-of-custody forms that were received with the samples. Stage 2A data validation consists of checking technical holding times; and a completeness audit to ensure that all sample results are present as requested by the chain-of-custody and that QC results are within specified method criteria. If data validation indicates significant quality problems, additional data validation will be recommended in the report and subsequently performed. Quality problems can include, but are not limited to, holding time exceedances; QC samples that are outside of specified control limits or frequencies; detection of common laboratory contaminants at greater than five times the MDLs; or other indications that the laboratory may not be adhering to proper quality control protocol. All of the data will be assessed by QA personnel under the QA Manager's direction for overall data usability and accuracy, taking into consideration sample collection, handling, QC data, and results of statistical analyses on the data as described above.

9.1.1.2 QC Documentation

Laboratory data will be screened for the inclusion and frequency of the necessary QC supporting information (detection limit verification, reagent blanks, duplicates, spikes, etc.). QC information not included or of insufficient frequency is cause to designate the affected measurement data as questionable or invalid. Requests for reanalysis for additional QC supporting information can be made at this point.

9.1.1.3 Corrective Action

The need for corrective action will be considered for all types of methods used if any of the above QC measures do not meet criteria as specified in the applicable method or this QAPP.

If QC data are outside established control limits and it is recognized that the laboratory is operating according to protocol and no error or anomaly has occurred during the

sample preparation and analysis, the only meaningful corrective action is re-extraction and re-analysis.

9.1.2 Data Validation of Field Measurement Data

Review of data obtained from the field, such as pH, dissolved oxygen (DO), turbidity, and temperature, taken during the compliance monitoring activities will be performed by the qualified field personnel. Validity of all data will be determined by checking calibration procedures utilized in the field and by comparing the data to previous measurements obtained at the specific site. Large variations will be evaluated in association with changes in local conditions and general trends. Variations in data which cannot be explained will be assigned a lower level of validity and will be used as needed. The qualified field personnel will summarize the data obtained from field measurements and will include this information in the Daily Logs.

9.1.3 Reconciliation with Data Quality Objectives

The QA manager will reconcile results obtained from the project with the requirements specified in Tables 3a and 3b of this QAPP. Assessment of data for precision, accuracy, and completeness will be in accordance with the quantitative definitions in Section 4.2.

9.2 Final Reporting and Report Archival

Once the data validation process and the assessment of usability of the data is completed, new data generated for the project will be entered into the project database. Data will be made available for analysis by the Project Coordinator, Supervising Contractor, and other authorized personnel. Copies of all analytical data and/or final reports will be retained in the laboratory files and will be stored on computer disks for a minimum of five years.

In accordance with the SOW (Sections 7.7 (d) 9 and 8.2), SWDs will submit to EPA and DTSC all sampling and tests results and other data in connection with the implementation of the CD. Analytical data, whether validated or not, will be submitted 45 days after the sample shipment to the laboratory or 14 days after receipt of analytical results from the laboratory, whichever occurs first.

10. DATA MANAGEMENT

Data management operations include data recording, validation, transformation, transmittal, reduction, analysis, tracking, storage and retrieval.

Calscience will provide laboratory analytical data in electronic data deliverable (EDD) format in addition to hard copy reports. In accordance with the SOW (Section 7.4 (a)), sampling and monitoring data will be submitted in EDD format acceptable to EPA. The proposed EDD format is shown in Appendix C.

Upon receipt from the laboratory, the analytical report and EDD will be entered into the project's data validation tracking system, which allows the data to be tracked from receipt, through validation, to data loading and storage. The electronic data will be imported into the database system concurrent with the data validation process. The database will be updated with validated data after validation of the laboratory data is complete. Data collected in the field will also be entered into the system and integrated with laboratory data.

As data are loaded into the system, a variety of quality checks are performed to ensure data integrity. These checks include:

- Audits to ensure that laboratories reported all requested analyses;
- Checks that all analytes are consistently and correctly identified;
- Reviews to ensure that units of measurement are provided and are consistent;
- Queries to determine that any codes used in the database are documented properly;
- Reports to review sample definitions (depths, dates, locations);
- Reviewing manually entered data against the hard-copy original; and
- Reports to review groupings of sampling locations and coordinate systems

Records of the checks will be maintained in the project file. At a minimum, the database will contain the following fields:

- Sample identifier;
- Sample location;

- Sample media type;
- Sampling date;
- Analysis date;
- Laboratory analysis identifier;
- Analyte name;
- Concentration value;
- Measurement units; and
- Data qualifiers.

The data will be considered final when data validation is complete and any required data qualifiers have been added to the database. Any changes made to the database after finalization will be documented, including a description of the change, date of change, person responsible, and reason for change. Once all data quality checks are performed, the data will be exported to a variety of formats to meet project needs. Cross-tab tables showing concentrations by sample location will be prepared. Data can be accessed by a variety of mapping and visualization tools. The project database will be maintained on a secure network drive which is backed up regularly. Access to the database will be limited to authorized project personnel and the ability to view and/or add or change data will be granted to only those individuals identified and trained to perform those tasks.

A sample cross reference list correlating sample names or numbers to well identities, blanks, duplicates, etc. will be provided to the EPA along with the EDDs.

11. AUDIT PROCEDURES

In accordance with SOW (Section 7.7 (d), 1), EPA will be allowed access, without prior notice and during regular business hours, to any laboratory premises where analysis or testing is being conducted. Personnel will be available for interview and laboratory records, equipment, procedures, and other items necessary will be available for audit of the laboratory's performance.

Under the responsibility of the laboratory QA manager, internal audits will also be performed. Performance and system audits will be carried out as presented below, and additional audits will be performed if problems are discovered. System audits are qualitative reviews of project activities to check that the overall QA program is functioning properly. Performance audits are quantitative checks on different aspects of internal support or project work, and are most appropriate for environmental sampling and analysis activities.

The Project Coordinator oversees the project performance to ensure that the internal quality control procedures are being followed. The Project Coordinator or her/his designee will perform at least one internal evidentiary system audit during the project. Evidentiary audits are checks on all of the project documentation that could potentially be required for legal proceedings. After the audit, the Project Coordinator will notify the QA manager of any deficiencies found and the proposed corrective measures. A copy of the audit notification will also be maintained in the project file.

The field audits will be performed by personnel selected by the QA manager. A field performance audit will be performed during the field activities to verify that QA/QC procedures are being followed. The auditor will compare the sampling, collection and documentation procedures as stated in project documents to what is actually being performed in the field. Field personnel will be notified of issues while the audit is being conducted. Discrepancies will be noted and the field personnel will be notified and corrections will be implemented.

The QA manager will select personnel to perform the laboratory system audit when necessary. If problems arise, a laboratory system audit will be conducted to ensure that the laboratory can and does perform analyses in a manner consistent with the requirements of this QAPP and with the laboratory's internal QA/QC protocols. The laboratory personnel will be notified of issues while the audit is conducted and

corrective measures will be developed. Subsequent to the audit, the QA manager will develop an audit report to summarize the findings, including those areas found to be non-conforming, and also the proposed corrective measures. The summary will be prepared in memo form and copied to the project files.

The EPA will be notified when internal evidentiary system audits, field performance audits, or laboratory system audits are performed. The results of these audits will be made available to EPA upon request.

12. CORRECTIVE ACTION

The QA program serves to prevent problems, but also identifies and corrects those that exist. Usually these problems require immediate corrective action or long-term corrective action.

12.1 Corrective Action for Routine Activities

Problems or deficiencies found during normal routine activities will be resolved by implementing corrective action as part of normal operating procedures by staff. Corrective actions of this type will be noted in the field documentation or per the laboratory protocol for documenting corrective actions. No other formal documentation is necessary unless further corrective action is required. If normal procedures do not solve the problem, the staff will document the problem in a formal memo addressed to the QA manager and copied to the project file.

12.2 Corrective Action for Field Activities

The corrective action system used during the field activities is designed to identify the problems and solve them efficiently. The QA manager is responsible for the direction of this system and receives full support from management for its implementation. The essential steps are:

- Identify and define the problem;
- Assign responsibility for investigating the problem;
- Determine a corrective action to eliminate the problem;
- Assign and accept responsibility for implementing the corrective action;
- Implement the corrective action;
- Verify that the corrective action has solved or eliminated the problem; and
- Document the problem identified, the corrective action taken, and its effectiveness in eliminating the problem.

12.3 Corrective Action Resulting from QA Audits

Problems or deficiencies encountered during a QA audit will be corrected. The QA manager, along with the project manager, is responsible for completion of appropriate corrective action. The procedures used to carry out the corrective action will be:

- Auditor verbally notifies the QA manager and field personnel during audits where deficiencies or problems are found;
- QA manager implements the necessary corrective action as soon as possible; and
- QA manager distributes the audit report promptly.

13. REFERENCES

American National Standard, 1995. *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Program.* 5 January.

CDM Smith, 2016. Remedial Design Work Plan, Omega Corporation Superfund Site, Operable Unit 2, Whittier California. In preparation, estimated September 2016.

Geosyntec, 2016a. Leading Edge Investigation Work Plan, Omega Corporation Superfund Site, Operable Unit 2, Whittier California. In preparation, estimated September 2016.

Geosyntec, 2016b. Work Area Groundwater Monitoring Plan, Omega Corporation Superfund Site, Operable Unit 2, Whittier California. In preparation, estimated 30 August 2016.

Hargis and Associates [H+A], 2016. Pre-Design Investigation Work Plan, Omega Corporation Superfund Site, Operable Unit 2, Whittier California. In preparation, estimated September 2016.

United States Environmental Protection Agency [EPA], 2001. Region 9 Superfund Data Evaluation/Validation Guidance, R9QA/006.1. Draft. December

EPA, 2002. Guidance for Quality Assurance Project Plans, QA/G-5, EPA/240/R 02/009. December.

EPA, 2004. Region 9 Sampling and Analysis Plan Template Version 3, Brownfields Projects. R9QA/006. Appendix C. June.

EPA, 2005a. Uniform Federal Policy for Quality Assurance Project Plans, Parts 1-3, EPA/505/B-04/900A though 900C. March.

EPA, 2005b. Policies and Procedures Manual, National Enforcement Investigations Center. EPA-330/9-97-002R. June.

EPA, 2006a. Guidance on Systematic Planning Using the Data Quality Objectives Process (QA/G-4). EPA/240/B/001. February.

EPA, 2006b. Requirements for Quality Management Plans (QA/R-2), (EPA/240/B-01/002 2001). March 2001. Re-issued May.

EPA, 2006c. EPA Requirements for Quality Assurance Project Plans, QA/R-5, EPA/240/B-01/003. March 2001. Re-issued May.

EPA, 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use, EPA 540-R08-005. January.

EPA, 2011. Interim Action Record of Decision, Omega Chemical Corporation Superfund Site, Operable Unit 2. Los Angeles County, California. 20 September.

EPA, 2014a. National Functional Guidelines for Superfund Organic Methods Data Review. EPA-540-R-014-002. August.

EPA, 2014b National Functional Guidelines for Superfund Inorganic Methods Data Review EPA-540-R-013-001. August.

EPA, 2015a. Remedial Design/Remedial Action Statement of Work, Operable Unit 02, Omega Chemical Corporation Superfund Site, Los Angeles County, State of California. 24 November.

EPA, 2015b. Contract Laboratory Program Statement of Work for Organic Superfund Methods. Multi-Media, Multi-Concentration. SOM02.3. September.

EPA, 2015c. Contract Laboratory Program Statement of Work for Inorganic Superfund Methods. Multi-Media, Multi-Concentration. ISM02.3. September.

EPA, 2016. Consent Decree regarding Operable Unit 2 at the Omega Chemical Corporation Superfund Site, Case 2:16-cv-02696 Document 4-1. Filed with United States District Court, Central District of California, Western Division. 20 April.

TABLES

Table 1a - Data Quality Objectives for Groundwater Monitoring Omega Superfund Site Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to monitor groundwater chemistry and movement within OU2 in the period between the Consent Decree entry and remedy operation.**	
Step 2 - Principal Study Goals	*Principal Study Goals*	1. Monitor the horizontal and vertical groundwater gradients in wells within the monitoring network.	2. Monitor the distribution of COCs in wells within the monitoring network.
	Potential Outcomes	Measure groundwater elevations in the Work Area monitoring wells to evaluate the horizontal groundwater gradients in the Work Area and the vertical groundwater gradients at monitoring well clusters.	Collect samples for laboratory analysis to obtain COC data from the Work Area monitoring wells to further characterize the distribution of COCs in the Work Area
Step 3 - Inputs to the Decision	*Needed Information*	Annual depth to water measurements in the Work Area monitoring wells and top of casing point of reference elevation from surveying of the Work Area monitoring wells	Analytical data of Main COC concentrations at Work Area monitoring wells: TCE, PCE, Freon 11, Freon 113, 1,1-DCE, cis-1,2-DCE, chloroform, carbon tetrachloride, 1,1-DCA, 1,2-DCA, 1,1,1-TCA, 1,4-dioxane, and hexavalent chromium
	Source of Needed Information or Data	Depth-to-water measurement performed during annual monitoring events and top of casing point of reference elevation data from surveying of the Work Area monitoring wells upon well completion	Groundwater samples collected annually from Work Area monitoring wells
	Action Levels µg/L	NA	Maximum Contaminant Levels and Notification Levels MCLs: TCE (5µg/L), PCE (5µg/L), Freon 11 (150µg/L), Freon 113 (1,200µg/L), 1,1-DCE (6µg/L), cis-1,2-DCE (6µg/L) chloroform (80µg/L*), carbon tetrachloride (0.5µg/L), 1,1-DCA (5µg/L), 1,2-DCA (0.5µg/L), 1,1,1-TCA (200µg/L), and hexavalent chromium (10µg/L) NL: 1,4-dioxane (1µg/L)
	Field Methods	Water level measurements and surveying at Work Area monitoring wells	Groundwater sampling from Work Area monitoring wells
	Analytical Methods	NA	VOCs by USEPA Method 8260B Hexavalent chromium by USEPA Method 218.6 1,4-dioxane by USEPA Method 8270C SIM
Step 4 - Study Boundaries	***Target Population***		
	Monitoring well locations (MW1 through MW32; new wells installed as part of the PDI; Koontz and Hawkins wells; new wells installed as part of the LEI and PDI) that will characterize the groundwater gradients within OU2.	Monitoring well locations (MW1 through MW32; Koontz and Hawkins wells; new wells installed as part of the LEI) that will characterize the distribution of contaminated groundwater within OU2. Groundwater samples will be collected in a sufficient volume to analyze for compounds and constituents listed in Step 3.	
	Spatial Boundaries		
	The OU2 Work Area is defined in Attachment C of the Consent Decree. Monitoring wells and depths to be monitored include: MW1 through MW32 and new wells installed by the SWDs as part of the PDI, all screened depth intervals; Koontz and Hawkins wells, all screened depth intervals; new wells installed by the SWDs as part of the LEI, all screened intervals to a depth of 500 feet.		
	Temporal Boundaries		
	To be initiated upon EPA approval of the Work Area Monitoring Plan and conducted annually until the NE/CE Remedial Action is operational. New LEI and PDI monitoring wells to be monitored in accordance with LEI and PDI Work Plans until respective reports submitted to EPA, then monitored annually as part of Work Area Monitoring Plan until the NE/CE Remedial Action is operational.		
	Potential Practical Constraints		
	Well access constraints, damaged wells, insufficient water in wells for sampling		
Step 5 - Decision Rules/Analytic Process	***Parameter that Characterizes Population of Interest***		
	The parameters that characterize the population of interest are individual data points (water levels and COC concentrations) measured at the Work Area monitoring wells		

Table 1a - Data Quality Objectives for Groundwater Monitoring Omega Superfund Site Operable Unit 2

Step 5 - Decision Rules/Analytic Process (Continued)	***Action Levels (µg/L) for Study***	
	NA	Action levels are presented in Step 3.
	Reporting Limits (µg/L)	
	NA	The reporting limits are lower than or equal to the action levels (Step 3). RLs: TCE (0.50µg/L), PCE (0.50µg/L), Freon 11 (0.50µg/L), Freon 113 (0.50µg/L), 1,1-DCE (0.50µg/L), cis-1,2-DCE (0.50µg/L), chloroform (0.50µg/L), carbon tetrachloride (0.50µg/L), 1,1-DCA (0.50µg/L), 1,2-DCA (0.50µg/L), 1,1,1-TCA (0.50µg/L), 1,4-dioxane (1.0µg/L), and hexavalent chromium (1.0µg/L)
	Analytic Process/Decision Rule	
	Depths to groundwater will be measured to the nearest one hundredth of one foot (0.01 foot). Groundwater elevations will be calculated using the depth to water measurements, and top of casing surveyed elevations for the monitoring wells. The top of casing elevations of the monitoring wells must be surveyed relative to mean sea level to the nearest 0.01 foot by a State of California Licensed Land Surveyor. The depths to groundwater and calculated groundwater elevations in each monitoring well will be presented in tables and figures to evaluate the direction of the horizontal and vertical gradients. Horizontal gradients across the Work Area will be calculated for the water table interval and presented on potentiometric surface maps, whereas vertical gradients will be presented in tabular format for individual well clusters.	Concentrations of Main COCs (TCE, PCE, Freon 11, Freon 113, 1,1-DCE, cis-1,2-DCE, chloroform, carbon tetrachloride, 1,1-DCA, 1,2-DCA, 1,1,1-TCA, 1,4-dioxane, and hexavalent chromium) will be presented in tables and select figures. Time series graphs of selected Main COCs concentrations (PCE, TCE, 1,1-DCE, cis-1,2-DCE, 1,1-DCA, 1,2-DCA, 1,4-dioxane, and hexavalent chromium) that represent the extent of contaminated groundwater will be developed.
Step 6 - Tolerable Limits on Decision Rules	Acceptance criteria include confirmation that measurements are collected accurately and preparing legible and accurate field notes. Errors will be minimized by adhering to the field QA/QC protocols established in the QAPP (Appendix A) and FSP (Appendix B).	Acceptance criteria include confirmation that laboratory data are: (1) representative of the chemical conditions that exist, (2) comparable to subsequent or previously collected data, (3) complete to the extent that necessary conclusions may be obtained, and (4) of known statistical significance in terms of precision and accuracy, at the levels that are appropriate for evaluating COC distribution. Errors will be minimized by adhering to the field QA/QC protocols established in the QAPP (Appendix A) and FSP (Appendix B).
Step 7 - Plan for Obtaining Data	Water levels will be measured manually using a QED®, Solinst® or comparable electric water level sounder. Pressure transducers and data loggers may also be installed and used to record water levels over an extended period.	Groundwater samples will be collected using low-flow sampling procedures with either a submersible pump or bladder pump. Each well will be purged, and field parameters will be monitored during purging. Samples will be collected after field parameters have stabilized as described in the Water Quality Parameter Measurements Standard Operating Procedure (SOP) included in the FSP. All samples from the monitoring wells will be analyzed for VOCs by EPA Method 8260B; hexavalent chromium by EPA Method 218.6; and 1,4-dioxane by EPA Method 8270C SIM. Field and laboratory QA/QC samples will be collected and analyzed.

Table 1a - Data Quality Objectives for Groundwater Monitoring Omega Superfund Site Operable Unit 2

Notes:

* - Total trihalomethanes = Bromodichloromethane, Bromoform, Chloroform, Dibromochloromethane

μg/L: micrograms per liter
1,1-DCA: 1,1-Dichloroethane
1,1-DCE: 1,1-Dichloroethene
1,1,1-TCA: 1,1,1-Trichloroethane
1,2-DCA: 1,2-Dichloroethane
cis-1,2-DCE: cis-1,2-Dichloroethene
COCs: chemicals of concern
EPA: United States Environmental Protection Agency
FSP: Field Sampling Plan
Freon 11: trichlorofluoromethane
Freon 113: 1,1,2-Trichloro-1,2,2,-trifluoroethane
LE: Leading Edge
LEI: Leading Edge Investigation
Main COCs: main chemicals of concern
MCLs: maximum contaminant levels
NA: not applicable
NE/CE: Northern Extraction/Central Extraction
NL: notification level
OU2: Operable Unit 2
PCE: Tetrachloroethene
PDI: Pre-Design Investigation
QAPP: Quality Assurance Project Plan
QA/QC: Quality Assurance/Quality Control
RL: Reporting Limit
TCE: trichloroethene
VOCs: Volatile Organic Compounds
WAMP: Work Area Monitoring Plan

References

http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/dwregulations-2016-06-14.pdf
Drinking Water Notification Levels and Response Levels: An Overview. Division of Drinking Water State Water Resources Control Board. February 4, 2015
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf

Table 1b - Data Quality Objectives for Leading Edge Investigation Omega Superfund Site Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry and vertical gradients at three locations within the LE Area as specified in the SOW to a depth of 500 feet bgs.**			
Step 2 - Principal Study Goals	*Principal Study Goals*	1. Determine the appropriate screen intervals for the wells in each LEI monitoring well cluster.	2. Characterize the vertical distribution of COCs in the LEI monitoring wells.	3. Characterize the vertical groundwater gradients in the LE Area.	
	Potential Outcomes	Select up to five screen interval depths for the installation of monitoring wells at each LEI monitoring well cluster location	Collect samples for laboratory analysis to obtain COC data from the LEI monitoring wells to further characterize the vertical extent of COCs in the LE Area	Measure groundwater elevations in the LEI monitoring wells and Koontz Well to evaluate the vertical gradients at each monitoring well cluster	
Step 3 - Inputs to the Decision	*Needed Information*	Lithologic logs including field observations of drill rig behaviors and geophysical logs; natural gamma; spontaneous potential, 16-inch normal resistivity, 64-inch normal resistivity, lateralog-3, and caliper/borehole volume at an exploratory boring at each LEI monitoring well cluster location. The existing hydrogeologic CSMs including the LE area prepared by EPA, DWR, and USGS.	Analytical data of COC concentrations at LEI monitoring wells including: TCE, PCE, Freon 11, Freon 113, 1,1-DCE, cis-1,2-DCE, chloroform, carbon tetrachloride, 1,1-DCA, 1,2-DCA, 1,1,1-TCA, 1,4-dioxane, and hexavalent chromium.	Depth to water and top of casing point of reference elevation at LEI monitoring wells and Koontz Well	
	Source of Needed Information or Data	Field notes on lithologic logging of borings at LEI monitoring well cluster locations. Geophysical logs of the exploratory boring at each LEI well cluster location.	Groundwater samples collected for three quarterly monitoring events from LEI monitoring wells following installation	Depth to water measurements performed in the LEI monitoring well clusters during three quarterly monitoring events following installation. Water levels collected with transducer data for a period of at least one month in the LEI monitoring well clusters and the Koontz well cluster.	
	Action Levels	NA	MCLs: TCE (5µg/L), PCE (5µg/L), Freon 11 (150µg/L), Freon 113 (1,200µg/L), 1,1-DCE (6µg/L), cis-1,2-DCE (6µg/L), chloroform (80µg/L*), carbon tetrachloride (0.5µg/L), 1,1-DCA (5µg/L), 1,2-DCA (0.5µg/L), 1,1,1-TCA (200µg/L), and hexavalent chromium (10µg/L) NL: 1,4-dioxane (1µg/L)	NA	
	Field Methods	Lithologic logging of drill cuttings. observations of drill rig behavior including speed and drill chatter, and geophysical logging	Groundwater sampling from LEI monitoring wells	Water level measurements and surveying at LEI monitoring wells	Collection of pressure transducer data and surveying at LEI monitoring wells
	Analytical Methods	Geophysical logs: natural gamma; spontaneous potential, 16-inch normal resistivity, 64-inch normal resistivity, lateralog-3, and caliper/borehole volume	VOCs by EPA Method 8260B Hexavalent chromium by EPA Method 218.6 1,4-dioxane by EPA Method 8270C SIM	NA	
Step 4 - Study Boundaries		***Target Population***			
		Coarse grained depth intervals up to 500 ft bgs in the LEI monitoring well cluster locations	Three LEI monitoring well clusters that will characterize the distribution of contaminated groundwater in the LE Area up to 500 feet bgs. Groundwater samples will be collected in a sufficient volume to analyze for compounds and constituents listed in Step 3.	The three LEI monitoring well clusters for three quarters of water level measurements and the LEI and Koontz well cluster for transducer data collection.	
		Spatial Boundaries			
		The spatial boundaries for the LEI are specified in Attachment C of the Consent Decree. Monitoring wells and depths to be monitored include three new well clusters installed as part of the LEI, all screened intervals up to a depth of 500 feet.			

Step 4 - Study Boundaries (continued)	***Temporal Boundaries***			
	To be initiated upon EPA approval of the LEI Work Plan	To be initiated upon completion of installation and development at each LEI monitoring well cluster and conducted for three quarters.	To be initiated upon completion of installation and development at each LEI monitoring well cluster. Water level measurements to be conducted for three quarters.	To be initiated upon EPA approval of the LEI work plan. Each well cluster to be monitored for a period of at least one month.
	Potential Practical Constraints			
	Obtaining access and permits to drill and install the LEI monitoring wells, the locations of buildings and utilities, city and/or county regulations on work hours	Well access constraints, damaged wells, insufficient water in wells for sampling		
Step 5 - Decision Rules/Analytic Process	***Parameter that Characterizes Population of Interest***			
	The parameters that characterize the population of interest are individual data points (water levels and COC concentrations) measured at LEI monitoring wells			
	Action Levels for Study			
	NA	Action levels are presented in Step 3.	NA	
	Reporting Limits			
	NA	The reporting limits are lower than or equal to the action levels (Step 3): TCE (0.50µg/L), PCE (0.50µg/L), Freon 11 (0.50µg/L), Freon 113 (0.50µg/L), 1,1-DCE (0.50µg/L), cis-1,2-DCE (0.50µg/L), chloroform (0.50µg/L), carbon tetrachloride (0.50µg/L), 1,1-DCA (0.50µg/L), 1,2-DCA (0.50µg/L), 1,1,1-TCA (0.50µg/L), 1,4-dioxane (1.0µg/L), and hexavalent chromium (1.0µg/L)	NA	
	Analytic Process/Decision Rule			
	The deepest well in LEI Monitoring Well Clusters 1 and 2 will be screened in the deepest coarse grained layer greater than 10 feet in thickness observed in the exploratory boring to a maximum depth of 500 feet. The deepest coarse grained layer will be identified by the California Professional Geologist supervising the work based on review of the exploratory boring lithologic and geophysical logs. A brief transmittal will be prepared to convey the selected well depth intervals and supporting data to EPA for review and approval.	Concentrations of COCs for the monitoring wells in the three LEI monitoring well clusters will be compared to MCLs and NLs (Step 3).	Groundwater elevations for the monitoring wells in the three LEI monitoring well clusters will be presented in tables and figures.	
	Up to four additional well screen intervals will be selected at each of these two LEI monitoring well clusters to be screened in the coarse grained layers. These layers will be identified by the California Professional Geologist supervising the work based on review of the exploratory boring lithologic and geophysical logs for each LEI monitoring well cluster location and the hydrogeologic CSMs. A brief transmittal will be prepared to convey the selected well depth intervals and supporting data to EPA for review and approval.			
	Following installation of LEI Monitoring Well Clusters 1 and 2 and review of the data collected from these wells, the location of LEI Monitoring Well Cluster 3 will be proposed for EPA review and approval. The process for selecting the screened intervals for this cluster will proceed as above.			

Step 6 - Tolerable Limits on Decision Rules	Acceptance criteria include confirmation that field data are: (1) representative of the geophysical conditions that exist, (2) comparable to subsequent or previously collected data and consistent with the current understanding of the existing CSMs, (3) complete to the extent that necessary conclusions may be obtained, and (4) accurate at the levels that are appropriate for determining the location of coarse grained intervals for monitoring well installation. Errors will be minimized by adhering to the field QA/QC protocols established in the QAPP and FSP.	Acceptance criteria include confirmation that laboratory data are: (1) representative of the chemical conditions that exist, (2) comparable to subsequent or previously collected data, (3) complete to the extent that necessary conclusions may be obtained, and (4) of known statistical significance in terms of precision and accuracy, at the levels that are appropriate for evaluating COC distribution. Errors will be minimized by adhering to the field QA/QC protocols established in the QAPP and FSP.	Acceptance criteria include confirmation that measurements are collected accurately to within 0.01 foot by repeating the measurement at each well and preparing legible and accurate field notes. Errors will be minimized by adhering to the field QA/QC protocols established in the QAPP and FSP.
Step 7 - Plan for Obtaining Data	Up to five monitoring well screen intervals at each well cluster will be selected as described above. The monitoring well depths and screen intervals will be selected to be in the coarsest grained layers. Geophysical logs will be used to select a screen interval for the deepest monitoring well in each well cluster. After the deepest well is installed, the geophysical and boring logs will be used to select up to four additional monitoring wells at each well cluster.	Groundwater samples will be collected using low-flow sampling procedures with either a submersible pump or bladder pump. Each well will be purged, and field parameters will be monitored during purging. Samples will be collected after field parameters have stabilized as described in the Water Quality Parameter Measurements SOP included in the FSP. All samples from the monitoring wells will be analyzed for VOCs by EPA Method 8260B; hexavalent chromium by EPA Method 218.6; and 1,4-dioxane by EPA Method 8270C SIM. Field and laboratory QA/QC samples will be collected and analyzed.	Water levels will be measured manually using a QED®, Solinst® or comparable flat tape electric water level sounder. Pressure transducers and data loggers will also be installed and used to record water levels for a period of at least one month.

Notes:

* - Total trihalomethanes = Bromodichloromethane, Bromoform, Chloroform, Dibromochloromethane

µg/L: micrograms per liter
µg/kg: micrograms per kilogram
mg/L: milligrams per liter
mg/kg: milligrams per kilogram
1,1-DCA: 1,1-Dichloroethane
1,1-DCE: 1,1-Dichloroethene
1,1,1-TCA: 1,1,1-Trichloroethane
1,2-DCA: 1,2-Dichloroethane
cis-1,2-DCE: cis-1,2-Dichloroethene
COCs: chemicals of concern
CSMs: Conceptual Site Models
DWR: Department of Water Resources
EPA: Environmental Protection Agency
FSP: Field Sampling Plan
feet bgs: feet below ground surface
Freon 11: trichlorofluoromethane
Freon 113: 1,1,2-Trichloro-1,2,2,-trifluoroethane
LE: Leading Edge
LEI: Leading Edge Investigation
MCLs: maximum contaminant levels
NA: not applicable
NLs: notification levels
OU2: Operable Unit 2
PCE: tetrachloroethene
QA/QC: quality assurance/quality control
QAPP: Quality Assurance Project Plan
ROD: Record of Decision
SOP: standard operating procedure
SOW: Statement of Work
TCE: trichloroethene
USGS: United States Geological Survey
VOC: volatile organic compound

References

California Code of Regulation Title 22. Sections 64431, 64444, 64449, and 64533. Last updated June 14, 2016
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/dwregulations-2016-06-14.pdf
Drinking Water Notification Levels and Response Levels: An Overview. Division of Drinking Water State Water Resources Control Board. February 4, 2015
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry, hydraulic properties and nature of hydrostratigraphic units in the Remedial Design Work Area to support the Remedial Design of the Northern Extraction/Central Extraction (NE/CE) Area as specified in the SOW.**							
		(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?			
	Principal Study Questions	What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 2 - Principal Study Questions	*Goals*	COCs monitoring results from PDI and existing MWs define the extent of Main COCs exceeding MCLs or NLs in the vicinity of the CE Area target extraction area.	COCs monitoring results from PDI and existing MWs will define the extent of the high COCs concentration area in the vicinity of the NE Area target extraction area.	Hydraulic testing data from PDI and existing MWs will characterize the hydraulic conductivity within the area/depths targeted for hydraulic control in the NE/CE Areas.	Refer to (i) and (ii) AND Water level data from PDI and existing MWs provide characterization of direction of groundwater flow and gradients within the area/depth targeted for hydraulic control in the NE/CE Areas.	The lithologic and borehole geophysical logs in conjunction with water level elevations in PDI and existing MWs within the RDWA will provide refinement to existing interpretations.	The permit requirements for each end use in conjunction with water quality sample results from PDI and selected existing MWs within the RDWA will be used to determine which constituents require treatment for each end use alternative.	Data from existing operators of reclaim and spreading basins are sufficient to complete capacity evaluations. Hydraulic testing in candidate reinjection areas and subsequent pilot injection testing are used to assess reinjection capacity in candidate reinjection areas.	The permit requirements for each end use in conjunction with water quality sample results from PDI and selected existing MWs within the NE/CE Area will be used to determine what treatment processes need to be included in treatment system.
	Potential Outcomes	(1) The results from 13 PDI MWs are sufficient to define the target extraction zone for the CE Area wellfield; or (2) additional deep PDI MW(s) are required.	(1) The results from 11 PDI MWs are sufficient to define the target extraction zone for the NE Area wellfield; or (2) additional PDI deep MW(s) are required.	(1) The results of hydraulic testing at PDI MWs are sufficient to support RD of the NE and CE Areas extraction wellfields; or (2) additional data collection is required to refine hydraulic properties.	Refer to (i) and (ii) AND: (1) The water level monitoring data are sufficient to characterize direction of groundwater flow and gradient; or (2) additional data collection is required to characterize direction of groundwater flow or gradient.	The information from PDI and existing borings and MWs will be used to refine understanding of hydrostratigraphic units in the RDWA.	(1) The results of water quality data are consistent and/or inconsistencies do not drive treatment requirements; or 2) additional sampling is required to resolve apparent anomalous data.	(1) the results indicate reinjection in respective area is viable; (2) the results indicate reinjection is not likely to sustain injection; in this case, the contingency injection area would need to be investigated or reinjection would be eliminated from end use consideration; or (3) another candidate potential injection area, (possibly including deep reinjection), would be investigated, or reinjection would be eliminated from end use consideration.	(1) The results of water quality data are consistent and/or inconsistencies do not drive treatment requirements; or 2) additional sampling is required to resolve apparent anomalous data.

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry, hydraulic properties and nature of hydrostratigraphic units in the Remedial Design Work Area to support the Remedial Design of the Northern Extraction/Central Extraction (NE/CE) Area as specified in the SOW.**							
		(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?			
	Principal Study Questions	What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 3 - Inputs to the Decision	*Needed Information*	COC data from MWs in vicinity of CE Area	COC data from MWs in vicinity of NE Area	Drawdown and recovery water level data from pumped/observation wells in the NE and CE Areas	Water level elevations in RDWA	Lithologic/geophysical logs from boreholes and water level elevations in MWs in RDWA. Refer to (iii) for water levels.	Water quality results for permitted constituents/compounds from MWs in vicinity of NE/CE Areas and in vicinity of candidate reinjection area(s) .	Drawdown and recovery data from MWs in vicinity of candidate reinjection area and water level build up in pilot injection well.	Water quality results for COCs, permitted constituents/compounds and selected constituents potentially affecting treatment system process from MWs in vicinity of NE/CE Areas.
	Source of Needed Information or Data	Water quality data from: 1) existing MWs from various databases/readily available groundwater assessment/monitoring data; and 2) data collected during the PDI.	Water quality data from: 1) existing MWs from various databases/readily available groundwater assessment/monitoring data; and 2) data collected during the PDI.	Hydraulic testing data from: 1) existing MWs from various databases/readily available site investigations conducted; and 2) data collected during the PDI.	Water level data and reference point elevations from: 1) existing MWs from various databases/readily available groundwater monitoring; and 2) data collected during the PDI.	Lithologic logs (and geophysical logs to the extent available) from: 1) existing monitor/production well boreholes from various databases/readily available site investigations; and 2) data collected during the PDI. Refer to (iii) for source of water levels.	Water quality data from: 1) existing MWs from various databases/readily available groundwater assessment/monitoring data; and 2) data collected during the PDI.	Hydraulic testing data from data collected during the PDI.	Water quality data from: 1) existing MWs from various databases/readily available groundwater assessment/monitoring data; and 2) data collected during the PDI.
	Action Levels	Decision on the vertical/lateral extent of COCs exceeding MCLs/NLs within the bounds of OU2 depicted in the 2011 ROD will be based on groundwater samples collected from PDI and selected existing MWs in the CE Area. Reporting limits for COCs should be below respective MCLs/NLs to delineate extent and depth of the CE Area wellfield. The decision criterion for additional deep PDI exploratory borehole/MW installation based on COC results from PDI MWs.	Decision on the vertical/lateral extent of higher concentration COCs will be based on groundwater samples collected from PDI and selected existing MWs in the NE Area. Reporting limits for COCs can be above respective MCLs/NLs; however, for consistency purposes with other data collected during the PDI the reporting limits should be below respective MCLs/NLs. The decision criterion for additional deep PDI exploratory borehole/MW installation based on COC results from PDI MWs.	No action levels are used in the hydraulic testing of MWs.	No action levels are used in water level data collection.	No action levels are used in definition of hydrostratigraphic units; professional judgement will be used to define hydrostratigraphic units.	Decision on selection of end use will be based on both the concentration of COCs and other water quality parameters (and capacity - item ivc). Reporting limits for COCs should be the lower of the following: respective MCLs/NLs; NPDES, or the WDR reporting limits.	Decision on selection of end use will be based on capacity (and water quality - item ivb). For reinjection, decision to test PDI MWs will be based on initial/confirmation samples from respective MWs and well yield during development. Decision to conduct pilot injection test will be based on hydraulic testing of PDI MWs in respective area.	Decision on treatment system components will be made based on the ability of the respective component to meet end use water quality treatment standards. Since there are multiple end uses being evaluated, the reporting limits for COCs and other water quality parameters should be the lower of the: MCL/NL; WDR reporting requirements; or NPDES reporting requirements.

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry, hydraulic properties and nature of hydrostratigraphic units in the Remedial Design Work Area to support the Remedial Design of the Northern Extraction/Central Extraction (NE/CE) Area as specified in the SOW.**							
		(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?			
	Principal Study Questions	What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 3 - Inputs to the Decision (continued)	*Field Methods*	Installation of PDI MWs in accordance with SOPs and FSP; groundwater sample collection from PDI and selected existing EPA/WRD MWs in accordance with SOPs and FSP.	Installation of PDI MWs in accordance with SOPs and FSP; groundwater sample collection from PDI and selected existing EPA/WRD MWs	Hydraulic testing in accordance with SOPs and FSP. Constant rate discharge tests in pumped well with water level monitoring in pumped and observation wells	Water level measurements in existing EPA/WRD in RDWA and PDI MWs. Water level measurement will consist of manual measurements in all EPA/WRD/PDI MWs in RDWA and pressure transducers in selected EPA/WRD and all PDI MWs. Water level elevations determined using water level measurements and surveyed reference point elevations.	Lithologic logs for PDI MWs to prepared in accordance wit SOPs. Geophysical logs of exploratory boreholes to be conducted in accordance with SOPs	Groundwater sample collection from PDI and selected existing EPA/WRD MWs	Hydraulic testing in accordance with SOPs and FSP. PDI MWs to be tested using constant rate discharge tests in pumped well with water level monitoring in pumped and observation wells. PDI pilot injection well to be tested using constant rate injection test and monitoring water levels in Pilot Injection well and nearby observation well.	Groundwater sample collection from PDI and selected existing EPA/WRD MWs
	Analytical Methods	MW installation, development and surveying to follow SOPs and associated QA requirements. COCs to be analyzed using EPA standard test methods in accordance with SOPs and QAPP. Analytical methods capable of meeting CA DDW DLRs for drinking water.	MW installation, development and surveying to follow SOPs and associated QA requirements. COCs to be analyzed using EPA standard test methods in accordance with SOPs and QAPP. Analytical methods capable of meeting CA DDW DLRs for drinking water.	All measurements are field measurements. Follow SOPs and associated QA requirements.	All measurements are field measurements. Follow SOPs and associated QA requirements.	Lithologic logs are based on field observations. Follow SOPs and associated QA requirements. Geophysical logs include: natural gamma; spontaneous potential, 16 inch normal resistivity, 64-inch normal resistivity, lateralog-3, and caliper/borehole volume	COCs to be analyzed using EPA standard test methods/ parameters included within discharge permits to be analyzed using EPA standard/commercially available specialty methods in accordance with SOPs and QAPP. Analytical methods capable of meeting CA DDW DLRs for drinking water, RWQCB DLRs for NPDES and/or screening levels.	All measurements are field measurements. Follow SOPs and associated QA requirements.	COCs to be analyzed using EPA standard test methods/ parameters included within discharge permits to be analyzed using EPA standard/commercially available specialty methods in accordance with SOPs and QAPP. Analytical methods capable of meeting CA DDW DLRs for drinking water, RWQCB DLRs for NPDES and/or screening levels.

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry, hydraulic properties and nature of hydrostratigraphic units in the Remedial Design Work Area to support the Remedial Design of the Northern Extraction/Central Extraction (NE/CE) Area as specified in the SOW.**						
		(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?			
	Principal Study Questions	What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 4 - Study Boundaries	***Target Population***								
		Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Groundwater and end use of treated groundwater	Groundwater	Groundwater and end use of treated groundwater
	Spatial Boundaries								
		The lateral investigation boundaries in the CE Area are the vicinity of Telegraph Road bounded on the east and west by the boundary of OU2 as depicted in the 2011 ROD. The vertical investigation boundary is defined by land surface at the top and the deepest MW screened in groundwater containing COCs exceeding MCL or NL at the bottom.	The lateral investigation boundaries in the NE Area are the vicinity of Sorensen Avenue bounded on the east and west by the boundary of OU2 as depicted in the 2011 ROD. The vertical investigation boundary is defined by land surface at the top and the deepest MW screened in groundwater containing elevated concentrations of COCs at the bottom. Decision criteria for delineating the bottom would be conservatively based on COCs exceeding MCLs or NLs.	For the CE and NE Areas the boundaries are similar to boundaries identified for both areas under item (i)	The lateral investigation boundaries are defined by the NE/CE Area (item i) and candidate reinjection area(s) (item ivc). The vertical investigation boundaries can vary by location within the lateral investigation boundaries and are defined by the water table at the top and the deepest existing or newly installed PDI MW in the respective area at the bottom.	The lateral investigation boundaries are defined by the NE/CE Area (item i) and candidate reinjection area(s) (item ivc). The vertical investigation boundaries can vary by location within the lateral investigation boundaries and are defined by the water table at the top and the deepest existing or newly installed PDI MW in the respective area at the bottom.	The lateral investigation boundaries are defined by the NE/CE Area (item i) and candidate reinjection area(s) (item ivc). The vertical investigation boundaries can vary by location within the lateral investigation boundaries and are defined by the water table at the top and the deepest existing or newly installed PDI MW in the respective area at the bottom.	The lateral investigation boundaries for the primary potential reinjection area are OU2 on the east, Interstate Highway 605 on the west, Washington Boulevard on the north, and Los Nietos Road on the south. The vertical investigation boundary is defined by land surface at the top and the base of the Gaspur aquifer at the bottom. See PDI DQO Appendix for lateral and vertical boundaries of contingency reinjection areas.	The lateral investigation boundaries are defined by the NE/CE Area (item i) and candidate reinjection area(s) (item ivc). The vertical investigation boundaries can vary by location within the lateral investigation boundaries and are defined by the water table at the top and the deepest existing or newly installed PDI MW in the respective area at the bottom.
	Temporal Boundaries								
		Conducted prior to initiating wellfield or treatment system design and completed before groundwater model predictive simulations.	Conducted prior to initiating wellfield or treatment system design and completed before groundwater model predictive simulations.	Conducted prior to initiating wellfield or treatment system design and completed before groundwater model calibration.	Throughout PDI. Conducted prior to initiating wellfield or treatment system design and completed before groundwater model calibration.	Conducted prior to initiating wellfield or treatment system design and completed before completing groundwater model construction.	Conducted prior to initiating wellfield or treatment system design and completed before groundwater model predictive simulations.	Conducted prior to initiating wellfield or treatment system design and completed before groundwater model predictive simulations.	Conducted prior to initiating wellfield or treatment system design and completed before groundwater model predictive simulations.
	Potential Practical Constraints								
		Access to the desired locations for MW installation/maintaining access for testing and monitoring, and/or potential for inclement weather that could significantly delay data collection efforts. In addition, scheduling qualified drilling/development/pump setting contractors may be difficult given their current demand associated with the California drought.							
	Scale of Estimates								
		Water quality, water level, and hydraulic data can vary laterally and vertically. The vertical variability can be relatively great over relatively small vertical distances when compared to lateral variability over similar distances. It is anticipated that the NE Area and CE Area individual extraction wells will have screened intervals ranging from approximately 50 feet to 100 feet or more and most of the groundwater produced from these extraction wells will be from the coarse sediments. Therefore the PDI MWs will target one or multiple coarse sediment sequences that would likely comprise a subset of the extraction well screen. Given this, it is expected that PDI MWs will have screened intervals ranging from approximately 20 feet to 50 feet in length. The lateral variations in water quality in the vicinity of the NE A and CE Area wellfields will be assessed by installing MWs in the target vertical intervals with lateral separation of approximately 1,000 feet transverse to the direction of groundwater flow, to estimate lateral variations in water quality across the width of the target extraction wellfields in the NE and CE Areas.							

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

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	Principal Study Questions	(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?		
		What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 5 - Decision Rules/Analytic Process		***Parameter that Characterizes Population of Interest***						
		Geometric mean of water quality data collected during the PDI from each individual MW		Individual data points			Average of available data for each individual MW	Individual data points	Average of available data for each individual MW
		Action Levels for Study						
		See Step 3 Action Levels						
		Reporting Limits						
		See Step 3 Analytical Methods						
		Analytic Process/Decision Rule						
		Project team in consultation with EPA will incorporate existing and newly acquired PDI data collected in the CE Area to define the target extraction interval for this wellfield using: COC data and comparing to MCLs and NLs. See PDI DQO Appendix for more specific information.	Project team in consultation with EPA will incorporate existing and newly acquired PDI data collected in the CE Area to define the target extraction interval for this wellfield using: COC data and focusing on higher concentration areas. See PDI DQO Appendix for more specific information.	Project team will incorporate existing and newly acquired PDI data collected in the CE and NE Areas to refine estimates of transmissivity and hydraulic conductivity within the target extraction intervals for these wellfields. See PDI DQO Appendix for more specific information.	The project team will incorporate existing and newly acquired PDI data collected to refine estimates of hydraulic gradient and direction of groundwater flow within hydrostratigraphic units throughout the RDWA. See PDI DQO Appendix for more specific information.	The project team will incorporate existing and newly acquired PDI data collected to refine hydrostratigraphic units throughout the RDWA using lithologic, borehole geophysical and water level data. See PDI DQO Appendix for more specific information.	The project team in consultation with permitting agency will incorporate existing and newly acquired PDI data to identify compounds and constituents requiring treatment.	The project team in consultation with permitting agency and owners/operators of reclaim/spreading basins will incorporate existing and newly acquired PDI data to identify capacity of respective end use for accepting treated groundwater. For reinjection, this would include defining candidate target injection intervals for returning treated groundwater to the aquifers. See PDI DQO Appendix for more specific information.	The project team will incorporate existing and newly acquired PDI data collected to refine estimates of influent water quality for COCs and parameters pertinent to different end uses of treated groundwater (end use permitting requirements) to determine treatment system requirements. See PDI DQO Appendix for more specific information.
Step 6 - Tolerable Limits on Decision Rules		This step of the DQO process is generally not applicable to activities supporting PDI activities because the sampling design (i.e., locations for MW installation, hydraulic testing and ground water monitoring) was selected based on a review of existing hydrogeologic and geochemical data and is based on professional judgment. As such, the predominant quantitative variability is field and laboratory analyses measurement errors. Field and laboratory measurement errors are minimized by following Standard Operating Procedures (SOPs) for respective data collection activities as outlined in the FSP and QAPP.						

Table 1c - Data Quality Objectives for Pre-Design Investigation
Omega Superfund Site, Operable Unit 2

Step 1 - Problem Statement / Objective		**There is a need to evaluate the groundwater chemistry, hydraulic properties and nature of hydrostratigraphic units in the Remedial Design Work Area to support the Remedial Design of the Northern Extraction/Central Extraction (NE/CE) Area as specified in the SOW.**						
	Principal Study Questions	(i) What is the area and depths targeted for hydraulic control in the NE and CE Areas?		(ii) What is the hydraulic conductivity in the NE/CE Area capture zone? **(PDI DQO Appendix PS4)**	(iii) What is the location and extraction rates for NE/CE extraction wells?	(iv) Are there additional data required to support RD?		
		What is the lateral/vertical extent of COCs exceeding MCLs or NLs in the vicinity of the CE Area near Telegraph Road? **(PDI DQO Appendix PS1)**	What is the lateral/vertical distribution of the high COCs concentration area in the vicinity of the NE Area near Sorensen Avenue? **(PDI DQO Appendix PS2)**		Refer to (i) and (ii) AND: What is the direction of groundwater flow and gradient and how they vary through the water year? **(PDI DQO Appendix PS6)**	(iva) What is the nature of hydrostratigraphic units in the RDWA? **(PDI DQO Appendix PS1, PS2 and PS3)**	(ivb) What constituents require additional treatment to meet end use of treated groundwater? **(PDI DQO Appendix PS3 and PS7)**	(ivc) Are there capacity limitations to treated groundwater end use alternatives? **(PDI DQO Appendix PS5)**	(ivd) What treatment system components are required to meet selected end use? **(PDI DQO Appendix PS7)**
Step 7 - Plan for Obtaining Data		Collect groundwater samples for COC analysis from 13 PDI MWs at 5 locations (Tasks 2 and 3) and 6 existing EPA/WRD MWs at 2 locations (Task 6).	Collect groundwater samples for COC analysis from 11 PDI MWs at 3 locations (Tasks 2 and 3) and 15 existing EPA MWs at 4 locations (Task 6).	Conduct constant rate hydraulic tests at 24 PDI MWs at 8 locations in NE/CE Area (Task 5).	In RDWA measure water levels using transducers in 28 existing MWs at 11 locations (Task 1); measure water levels using transducers in 28 MWs at 12 locations (Task 6); and periodic manual measurements at 64 existing MWs at 29 locations and 28 PDI MWs at 12 locations (Task 6).	The NE/CE Area lithologic and borehole geophysical data will be conducted at 7 deep exploratory boreholes. Lithologic logs will also be conducted at 5 PDI MWs (one in CE and 4 in the primary candidate reinjection area). These data will be used in conjunction with water level data collected as part of item (iii).	Collect groundwater samples for medium list analyte group from 28 PDI MWs at 12 locations and 21 existing EPA/WRD MWs (Tasks 2, 3, 4 and 6) and collect groundwater samples for long list analyte group from at 6 MWs in NE Area, 6 MWs in CE Area and 4 MWs in reinjection area (Tasks 4 and 6).	Conduct constant rate hydraulic tests at 4 PDI MWs at 4 locations in NE/CE Area and conduct pilot injection test at one location (Task 5).	Collect groundwater samples for medium list analyte group from 28 PDI MWs at 12 locations and 21 existing EPA/WRD MWs (Tasks 2, 3, 4 and 6) and collect groundwater samples for long list analyte group from at 6 MWs in NE Area, 6 MWs in CE Area and 4 MWs in reinjection area (Tasks 4 and 6).

Acronyms:

2011 ROD: OU2 Interim Action Record of Decision, Sept. 20, 2011
2016 CD: Consent Decree lodged April 20, 2016 covering OU2
CE Area: Central extraction area
COC: Chemicals of Concern
DDW: Division of Drinking Water
DLRs: detection limits for reporting
DQO: Data Quality Objectives
EPA: U.S. Environmental Protection Agency
FSP: Field Sampling Plan for PDI
MCLs: maximum contaminant levels (EPA and California)
MW: monitor well
NE Area: Northern extraction area
NLs: Notification Levels, California State Water Resources Control Board
NPDES: National Pollution Discharge Elimination System
OU2: Operable Unit 2
PDI: Pre-Design Investigation
PS: PDI DQO problem statement
QAPP: Quality Assurance Project Plan
RD: Remedial Design
RDWA: Remedial Design Work Area
RWQCB: Regional Water Quality Control Board, Los Angeles
SOPs: standard operating procedures
SOW: Statement of Work, Appendix B to the 2016 CD
WDR: Waste Discharge Requirements
WRD: Water Replenishment District

TABLE 2

Main Compounds of Concern

Main Compounds of Concern (COCs)	
Volatile Organic Compounds	Trichloroethene (TCE)
	Tetrachloroethene / Perchloroethene (PCE)
	Trichlorofluoromethane (Freon 11)
	1,1,2-Trichloro-1,2,2,-trifluoroethane (Freon 113)
	1,1-Dichloroethene (1,1-DCE)
	cis-1,2-Dichloroethene (cis-1,2-DCE)
	chloroform
	carbon tetrachloride
	1,1-Dichloroethane (1,1-DCA)
	1,2-Dichloroethane (1,2-DCA)
	1,1,1-Trichloroethane (1,1,1-TCA)
Other	1,4-dioxane
	hexavalent chromium

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 100.2	Asbestos	1332-21-4	0.2	--	MFL	--	--	--	--
EPA 200.7	Aluminum	7429-90-5	12.4	50	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Antimony	7440-36-0	7.87	15	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Arsenic	7440-38-2	4.38	15	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Barium	7440-39-3	2.96	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Beryllium	7440-41-7	2.62	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Boron	7440-42-8	4.76	20	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Cadmium	7440-43-9	2.69	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Calcium	7440-70-2	11.8	100	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Chromium	7440-47-3	2.71	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Cobalt	7440-48-4	2.95	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Copper	7440-50-8	2.67	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Iron	7439-89-6	10.1	100	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Lead	7439-92-1	4.06	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Magnesium	7439-95-4	3.36	100	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Manganese	7439-96-5	2.7	5	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Molybdenum	7439-98-7	2.78	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Nickel	7440-02-0	2.98	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Potassium	7440-09-7	103	500	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Selenium	7782-49-2	6.99	15	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Silicon	7440-21-3	27.9	50	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Silver	7440-22-4	1.39	5	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Sodium	7440-23-5	103	500	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Strontium	7440-24-6	2.77	30	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Thallium	7440-28-0	2.91	15	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Vanadium	7440-62-2	2.44	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 200.7	Zinc	7440-66-6	3.52	10	µg/L	80 - 120	0 - 20	85 - 115	0 - 20
EPA 218.6	Chromium, Hexavalent	18540-29-9	0.041	0.20	µg/L	85 - 121	0 - 25	95 - 107	0 - 20
EPA 245.1	Mercury	7439-97-6	0.0453	0.2	µg/L	57 - 141	0 - 10	85 - 121	0 - 10
EPA 300.0	Chloride	16887-00-6	0.52	1.0	mg/L	80 - 120	0 - 20	90 - 110	0 - 15
EPA 300.0	Nitrate (as N)	14797-55-8	0.053	0.10	mg/L	80 - 120	0 - 20	90 - 110	0 - 15
EPA 300.0	Sulfate	14808-79-8	0.27	1.0	mg/L	80 - 120	0 - 20	90 - 110	0 - 15
EPA 300.0	Fluoride	16984-48-8	0.027	0.10	mg/L	80 - 120	0 - 20	90 - 110	0 - 15
EPA 314.0	Perchlorate	14797-73-0	0.41	2.0	µg/L	80 - 120	0 - 15	85 - 115	0 - 15

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 504.1	1,2-Dibromo-3-Chloropropane	96-12-8	0.0023	0.010	µg/L	65 - 135	0 - 25	70 - 130	0 - 20
EPA 504.1	1,2-Dibromoethane	106-93-4	0.0020	0.010	µg/L	65 - 135	0 - 25	70 - 130	0 - 20
SRL 524M-TCP	1,2,3-Trichloropropane	96-18-4	0.0013	0.0050	µg/L	70 - 130	0 - 20	80 - 120	0 - 20
EPA 1613	Dioxin (2.3.7.8-TCDD)	1746-01-6	0.157	5.0	pg/L	73 - 146	0 - 50	73 - 146	0 - 35
EPA 1613	13C-2,3,7,8-TCDD	76523-40-5	--	--	--	25 - 141	--	--	--
EPA 1625C (M)	N-Nitrosodimethylamine	62-75-9	0.003	0.010	µg/L	10 - 130	0 - 20	70 - 120	0 - 20
SM 2540 C	Solids, Total Dissolved	10-33-3	0.87	1.0	mg/L	80 - 120	0 - 20	80 - 120	0 - 20
SM 4500-CN E	Cyanide, Total	57-12-5	0.0070	0.020	mg/L	70 - 130	0 - 25	80 - 120	0 - 20
EPA 8015B (M)	TPH as Gasoline	8006-61-9	48	100	µg/L	68 - 122	0 - 18	78 - 120	0 - 10
EPA 8015B (M)	1,4-Bromofluorobenzene	460-00-4	--	--	--	38 - 134	--	--	--
EPA 8015B (M)	Methanol	67-56-1	0.032	0.10	mg/L	64 - 118	0 - 20	69 - 117	0 - 22
EPA 8015B (M)	Total Petroleum Hydrocarbons (C6-C44)	**	32	100	µg/L	--	--	--	--
EPA 8015B (M)	TPH as Diesel	68334-30-5	32	100	µg/L	55 - 133	0 - 30	75 - 117	0 - 13
EPA 8015B (M)	n-Octacosane	630-02-4	--	--	--	68 - 140	--	--	--
EPA 8015B (M)	TPH as Jet A	--	86	100	µg/L	55 - 133	0 - 30	75 - 117	0 - 13
EPA 8015B (M)	n-Octacosane	630-02-4	--	--	--	68 - 140	--	--	--
EPA 8081A	4,4'-DDD	72-54-8	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	4,4'-DDE	72-55-9	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	4,4'-DDT	50-29-3	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Aldrin	309-00-2	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endosulfan I	959-98-8	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endosulfan II	33213-65-9	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Alpha-BHC	319-84-6	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Beta-BHC	319-85-7	0.015	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Chlordane	57-74-9	0.17	0.50	µg/L	--	--	--	--
EPA 8081A	Delta-BHC	319-86-8	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Dieldrin	60-57-1	0.014	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endosulfan Sulfate	1031-07-8	0.015	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endrin	72-20-8	0.015	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endrin Aldehyde	7421-93-4	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Gamma-BHC	58-89-9	0.015	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 8081A	Heptachlor	76-44-8	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Heptachlor Epoxide	1024-57-3	0.013	0.050	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Kepone	143-50-0	0.026	0.10	µg/L	--	--	--	--
EPA 8081A	Lindane	58-89-9	0.030	0.10	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Methoxychlor	72-43-5	0.025	0.10	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Mirex	2385-85-5	0.029	0.10	µg/L	--	--	--	--
EPA 8081A	Toxaphene	8001-35-2	0.30	2.0	µg/L	--	--	--	--
EPA 8082	Aroclor-1016	12674-11-2	0.15	0.50	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8082	Aroclor-1221	11104-28-2	0.14	0.50	µg/L	--	--	--	--
EPA 8082	Aroclor-1232	11141-16-5	0.12	0.50	µg/L	--	--	--	--
EPA 8082	Aroclor-1242	53469-21-9	0.063	0.50	µg/L	--	--	--	--
EPA 8082	Aroclor-1248	12672-29-6	0.10	0.50	µg/L	--	--	--	--
EPA 8082	Aroclor-1254	11097-69-1	0.11	0.50	µg/L	--	--	--	--
EPA 8082	Aroclor-1260	11096-82-5	0.13	0.50	µg/L	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8151A	2,4-Dichlorophenoxyacetic acid	--	--	--	µg/L	--	--	--	--
EPA 8151A	2,4,5-TP (Silvex)	--	--	--	µg/L	--	--	--	--
EPA 8260B	1,1,1-Trichloroethane	71-55-6	0.19	0.50	µg/L	66 - 130	0 - 30	66 - 130	0 - 30
EPA 8260B	1,1,2,2-Tetrachloroethane	79-34-5	0.22	0.50	µg/L	67 - 132	0 - 25	67 - 132	0 - 25
EPA 8260B	1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	0.26	0.50	µg/L	52 - 145	0 - 35	52 - 145	0 - 35
EPA 8260B	1,1,2-Trichloroethane	79-00-5	0.32	0.50	µg/L	77 - 124	0 - 25	77 - 124	0 - 25
EPA 8260B	1,1-Dichloroethane	75-34-3	0.19	0.50	µg/L	63 - 144	0 - 32	63 - 144	0 - 32
EPA 8260B	1,1-Dichloroethene	75-35-4	0.20	0.50	µg/L	66 - 130	0 - 32	66 - 130	0 - 32
EPA 8260B	1,2,4-Trichlorobenzene	120-82-1	0.25	0.50	µg/L	71 - 128	0 - 26	71 - 128	0 - 26
EPA 8260B	1,2-Dichlorobenzene	95-50-1	0.17	0.50	µg/L	78 - 120	0 - 19	78 - 120	0 - 19
EPA 8260B	1,2-Dichloroethane	107-06-2	0.18	0.50	µg/L	72 - 130	0 - 25	72 - 130	0 - 25
EPA 8260B	1,2-Dichloropropane	78-87-5	0.24	0.50	µg/L	74 - 122	0 - 24	74 - 122	0 - 24
EPA 8260B	1,3-Dichloropropane	142-28-9	0.24	1.0	µg/L	74 - 128	0 - 21	74 - 128	0 - 21
EPA 8260B	1,3-Dichlorobenzene	541-73-1	0.17	0.50	µg/L	75 - 120	0 - 22	75 - 120	0 - 22
EPA 8260B	1,4-Dichlorobenzene	106-46-7	0.31	0.50	µg/L	78 - 120	0 - 21	78 - 120	0 - 21
EPA 8260B	2-Butanone	78-93-3	2.9	5.0	µg/L	55 - 138	0 - 45	55 - 138	0 - 45
EPA 8260B	2-Chloroethyl Vinyl Ether	110-75-8	3.1	5.0	µg/L	60 - 139	0 - 90	60 - 139	0 - 90
EPA 8260B	Acetone	67-64-1	3.5	10	µg/L	51 - 163	0 - 82	51 - 163	0 - 82
EPA 8260B	Acrolein	107-02-8	8.8	20	µg/L	70 - 130	0 - 35	70 - 130	0 - 35
EPA 8260B	Acrylonitrile	107-13-1	5.2	10	µg/L	65 - 149	0 - 89	65 - 149	0 - 89
EPA 8260B	Benzene	71-43-2	0.32	0.50	µg/L	77 - 121	0 - 21	77 - 121	0 - 21
EPA 8260B	Bromodichloromethane	75-27-4	0.20	0.50	µg/L	72 - 129	0 - 26	72 - 129	0 - 26
EPA 8260B	Bromoform	75-25-2	0.34	0.50	µg/L	61 - 140	0 - 22	61 - 140	0 - 22

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 8260B	Bromomethane	74-83-9	0.38	1.0	µg/L	63 - 140	0 - 36	63 - 140	0 - 36
EPA 8260B	c-1,2-Dichloroethene	156-59-2	0.24	0.50	µg/L	76 - 123	0 - 32	76 - 123	0 - 32
EPA 8260B	c-1,3-Dichloropropene	10061-01-5	0.18	0.50	µg/L	76 - 126	0 - 24	76 - 126	0 - 24
EPA 8260B	Carbon Disulfide	75-15-0	0.44	1.0	µg/L	27 - 170	0 - 36	27 - 170	0 - 36
EPA 8260B	Carbon Tetrachloride	56-23-5	0.22	0.50	µg/L	64 - 135	0 - 31	64 - 135	0 - 31
EPA 8260B	Chlorobenzene	108-90-7	0.14	0.50	µg/L	80 - 120	0 - 20	80 - 120	0 - 20
EPA 8260B	Chloroethane	75-00-3	0.34	0.50	µg/L	67 - 131	0 - 35	67 - 131	0 - 35
EPA 8260B	Chloroform	67-66-3	0.22	0.50	µg/L	75 - 126	0 - 20	75 - 126	0 - 31
EPA 8260B	Chloromethane	74-87-3	0.22	0.50	µg/L	54 - 143	0 - 41	54 - 143	0 - 41
EPA 8260B	Dibromochloromethane	124-48-1	0.24	0.50	µg/L	76 - 132	0 - 23	76 - 132	0 - 23
EPA 8260B	Diisopropyl Ether (DIPE)	108-20-3	0.24	0.50	µg/L	70 - 130	0 - 35	70 - 130	0 - 35
EPA 8260B	Ethanol	64-17-5	17	50	µg/L	73 - 139	0 - 27	73 - 133	0 - 30
EPA 8260B	Ethylbenzene	100-41-4	0.32	0.50	µg/L	78 - 120	0 - 23	78 - 120	0 - 23
EPA 8260B	Ethyl-t-Butyl Ether (ETBE)	637-92-3	0.22	0.50	µg/L	70 - 130	0 - 35	70 - 130	0 - 35
EPA 8260B	Methylene Chloride	75-09-2	0.38	1.0	µg/L	71 - 129	0 - 30	71 - 129	0 - 30
EPA 8260B	Methyl-t-Butyl Ether (MTBE)	1634-04-4	0.29	0.50	µg/L	57 - 144	0 - 31	57 - 144	0 - 31
EPA 8260B	Naphthalene	91-20-3	0.41	1.0	µg/L	55 - 159	0 - 30	55 - 159	0 - 30
EPA 8260B	o-Xylene	95-47-6	0.39	0.50	µg/L	74 - 122	0 - 24	74 - 122	0 - 24
EPA 8260B	p/m-Xylene	179601-23-1	0.24	0.50	µg/L	74 - 122	0 - 23	74 - 122	0 - 23
EPA 8260B	t-1,2-Dichloroethene	156-60-5	0.26	0.50	µg/L	67 - 129	0 - 35	67 - 129	0 - 35
EPA 8260B	t-1,3-Dichloropropene	10061-02-6	0.35	0.50	µg/L	71 - 127	0 - 22	71 - 127	0 - 22
EPA 8260B	Tert-Amyl-Methyl Ether (TAME)	994-05-8	0.24	0.50	µg/L	70 - 130	0 - 35	70 - 130	0 - 35
EPA 8260B	Tert-Butyl Alcohol (TBA)	75-65-0	4.1	10	µg/L	43 - 170	0 - 38	43 - 170	0 - 38
EPA 8260B	Tetrachloroethene	127-18-4	0.22	0.50	µg/L	72 - 119	0 - 24	72 - 119	0 - 24
EPA 8260B	Toluene	108-88-3	0.26	0.50	µg/L	78 - 120	0 - 25	78 - 120	0 - 25
EPA 8260B	Trichloroethene	79-01-6	0.23	0.50	µg/L	75 - 116	0 - 24	75 - 116	0 - 24
EPA 8260B	Trichlorofluoromethane	75-69-4	0.25	0.50	µg/L	62 - 146	0 - 36	62 - 146	0 - 36
EPA 8260B	Vinyl Chloride	75-01-4	0.27	0.50	µg/L	60 - 141	0 - 34	60 - 141	0 - 34
EPA 8270C	1,2 Diphenylhydrazine (as Azobenzene)	103-33-3	2.6	10	µg/L	50 - 130	0 - 20	50 - 130	0 - 20
EPA 8270C	2-Chlorophenol	95-57-8	2.3	10	µg/L	35 - 105	0 - 18	35 - 105	0 - 18
EPA 8270C	2,4-Dichlorophenol	120-83-2	2.5	10	µg/L	50 - 105	0 - 20	50 - 105	0 - 20
EPA 8270C	2,4-Dimethylphenol	105-67-9	2.4	10	µg/L	30 - 110	0 - 20	30 - 110	0 - 20
EPA 8270C	2,4-Dinitrophenol	51-28-5	13	50	µg/L	15 - 140	0 - 20	15 - 140	0 - 20
EPA 8270C	2,4-Dinitrotoluene	121-14-2	2.3	10	µg/L	50 - 120	0 - 36	50 - 120	0 - 36
EPA 8270C	2,4,5-Trichlorophenol	95-95-4	2.5	10	µg/L	10 - 150	0 - 20	20 - 145	0 - 20
EPA 8270C	2,4,6-Trichlorophenol	88-06-2	2.5	10	µg/L	50 - 115	0 - 20	50 - 115	0 - 20
EPA 8270C	2,6-Dinitrotoluene	606-20-2	2.4	10	µg/L	50 - 115	0 - 20	50 - 115	0 - 20
EPA 8270C	2-Methylphenol (o-cresol)	95-48-7	2.1	10	µg/L	10 - 150	0 - 20	20 - 145	0 - 20
EPA 8270C	2-Nitrophenol	88-75-5	2.6	10	µg/L	40 - 115	0 - 20	40 - 115	0 - 20

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 8270C	2-Chloronaphthalene	91-58-7	2.8	10	µg/L	50 - 105	0 - 20	50 - 105	0 - 20
EPA 8270C	3,3'-Dichlorobenzidine	91-94-1	2.6	25	µg/L	20 - 110	0 - 20	20 - 110	0 - 20
EPA 8270C	3/4-Methylphenol (m/p cresol)	65794-96-9	2.2	10	µg/L	10 - 150	0 - 20	20 - 145	0 - 20
EPA 8270C	3-Methyl-4-Chlorophenol	59-50-7	2.4	10	µg/L	45 - 110	0 - 40	45 - 110	0 - 40
EPA 8270C	4,6-Dinitro-2-Methylphenol	534-52-1	14	50	µg/L	40 - 130	0 - 20	40 - 130	0 - 20
EPA 8270C	4-Nitrophenol	100-02-7	1.6	10	µg/L	20 - 150	0 - 40	20 - 150	0 - 40
EPA 8270C	4-Bromophenyl-Phenyl Ether	101-55-3	2.7	10	µg/L	50 - 115	0 - 20	50 - 115	0 - 20
EPA 8270C	4-Chlorophenyl-Phenyl Ether	7005-72-3	2.7	10	µg/L	50 - 110	0 - 20	50 - 110	0 - 20
EPA 8270C	Acenaphthene	83-32-9	2.8	10	µg/L	45 - 110	0 - 11	45 - 110	0 - 11
EPA 8270C	Acenaphthylene	208-96-8	2.9	10	µg/L	50 - 105	0 - 20	50 - 105	0 - 20
EPA 8270C	Anthracene	120-12-7	3.0	10	µg/L	55 - 110	0 - 20	55 - 110	0 - 20
EPA 8270C	Benzidine	92-87-5	6.5	50	µg/L	50 - 130	0 - 20	50 - 130	0 - 20
EPA 8270C	Benzo (a) Anthracene	56-55-3	4.7	10	µg/L	55 - 110	0 - 20	55 - 110	0 - 20
EPA 8270C	Benzo (a) Pyrene	50-32-8	2.4	10	µg/L	55 - 110	0 - 20	55 - 110	0 - 20
EPA 8270C	Benzo (b) Fluoranthene	205-99-2	2.3	10	µg/L	45 - 120	0 - 20	45 - 120	0 - 20
EPA 8270C	Benzo (g,h,i) Perylene	191-24-2	2.5	10	µg/L	40 - 125	0 - 20	40 - 125	0 - 20
EPA 8270C	Benzo (k) Fluoranthene	207-08-9	3.2	10	µg/L	45 - 125	0 - 20	45 - 125	0 - 20
EPA 8270C	Bis(2-Chloroethoxy) Methane	111-91-1	2.5	10	µg/L	45 - 105	0 - 20	45 - 105	0 - 20
EPA 8270C	Bis(2-Chloroethyl) Ether	111-44-4	2.5	25	µg/L	35 - 110	0 - 20	35 - 110	0 - 20
EPA 8270C	Bis(2-Chloroisopropyl) Ether	108-60-1	3.2	10	µg/L	25 - 130	0 - 20	25 - 130	0 - 20
EPA 8270C	Bis(2-Ethylhexyl) Phthalate	117-81-7	3.2	10	µg/L	40 - 125	0 - 20	40 - 125	0 - 20
EPA 8270C	Butyl Benzyl Phthalate	85-68-7	2.5	10	µg/L	45 - 115	0 - 20	45 - 115	0 - 20
EPA 8270C	Chrysene	218-01-9	2.8	10	µg/L	55 - 110	0 - 20	55 - 110	0 - 20
EPA 8270C	Dibenz (a,h) Anthracene	53-70-3	2.5	10	µg/L	40 - 125	0 - 20	40 - 125	0 - 20
EPA 8270C	Diethyl Phthalate	84-66-2	2.8	10	µg/L	40 - 120	0 - 20	40 - 120	0 - 20
EPA 8270C	Dimethyl Phthalate	131-11-3	2.6	10	µg/L	25 - 125	0 - 20	25 - 125	0 - 20
EPA 8270C	Di-n-Butyl Phthalate	84-74-2	2.9	10	µg/L	55 - 115	0 - 20	55 - 115	0 - 20
EPA 8270C	Di-n-Octyl Phthalate	117-84-0	2.5	10	µg/L	35 - 135	0 - 20	35 - 135	0 - 20
EPA 8270C	Fluoranthene	206-44-0	3.1	10	µg/L	55 - 115	0 - 20	55 - 115	0 - 20
EPA 8270C	Fluorene	86-73-7	2.7	10	µg/L	50 - 110	0 - 20	50 - 110	0 - 20
EPA 8270C	Hexachlorobenzene	118-74-1	3.1	10	µg/L	50 - 110	0 - 20	50 - 110	0 - 20
EPA 8270C	Hexachloro-1,3-Butadiene	87-68-3	2.9	10	µg/L	25 - 105	0 - 20	25 - 105	0 - 20
EPA 8270C	Hexachlorocyclopentadiene	77-47-4	6.9	25	µg/L	50 - 130	0 - 20	50 - 130	0 - 20
EPA 8270C	Hexachloroethane	67-72-1	3.0	10	µg/L	30 - 95	0 - 20	30 - 95	0 - 20
EPA 8270C	Indeno (1,2,3-c,d) Pyrene	193-39-5	2.1	10	µg/L	45 - 125	0 - 20	45 - 125	0 - 20
EPA 8270C	Isophorone	78-59-1	2.5	10	µg/L	50 - 110	0 - 20	50 - 110	0 - 20
EPA 8270C	N-Nitroso-di-n-propylamine	621-64-7	2.4	10	µg/L	35 - 130	0 - 13	35 - 130	0 - 13
EPA 8270C	N-Nitrosodiphenylamine	86-30-6	2.8	10	µg/L	50 - 110	0 - 20	50 - 110	0 - 20
EPA 8270C	Nitrobenzene	98-95-3	3.0	25	µg/L	45 - 110	0 - 20	45 - 110	0 - 20
EPA 8270C	Pentachlorophenol	87-86-5	4.6	10	µg/L	40 - 115	0 - 40	40 - 115	0 - 40

Table 3a
Laboratory QC Control Limits (Water)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 8270C	Phenanthrene	85-01-8	2.9	10	µg/L	50 - 115	0 - 20	50 - 115	0 - 20
EPA 8270C	Phenol	108-95-2	2.1	10	µg/L	0 - 115	0 - 23	10 - 115	0 - 23
EPA 8270C	Pyrene	129-00-0	3.0	10	µg/L	50 - 130	0 - 20	50 - 130	0 - 20
EPA 8270C	Pyridine	110-86-1	3.0	10	µg/L	10 - 150	0 - 20	20 - 145	0 - 20
EPA 8270C (M) Isotope Dilution	1,4-Dioxane	123-91-1	0.28	1.0	µg/L	50 - 130	0 - 20	50 - 130	0 - 20
DHS LUFT	Organic Lead	--	0.117	0.300	mg/L	25 - 121	0 - 11	57 - 135	0 - 30

Notes:
-- - not applicable
µg/L - micrograms per liter
mg/L - milligram per liter
QC - quality control
CAS - Chemical Abstracts Service
EPA - Environmental Protection Agency
MDL - method detection limit
RL - reporting limit
LCS CL - laboratory check sample control limit
LCS RPD - laboratory check sample relative percent difference
MFL - million fibers per liter
MS CL - matrix spike control limit
MS RPD - matrix spike relative percent difference
TPH - total petroleum hydrocarbons

Table 3b
Laboratory QC Control Limits (Soil)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 300.0	Fluoride	16984-48-8	0.31	1.0	mg/kg	80 - 120	0 - 20	90 - 110	0 - 15
EPA/600/R-93/116	Asbestos	1332-21-4	<1.0	<1.0	%	--	--	--	--
EPA 1613	Dioxin (2,3,7,8-TCDD)	1746-01-6	0.0283	0.5	pg/g	73-146	0-50	73-146	0-35
EPA 6010B	Antimony	7440-36-0	0.149	0.750	mg/kg	50 - 115	0 - 20	80 - 120	0 - 20
EPA 6010B	Arsenic	7440-38-2	0.259	0.750	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Barium	7440-39-3	0.154	0.500	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Beryllium	7440-41-7	0.137	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Cadmium	7440-43-9	0.135	0.500	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Chromium	7440-47-3	0.142	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Cobalt	7440-48-4	0.148	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Copper	7440-50-8	0.135	0.500	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Lead	7439-92-1	0.132	0.500	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 7471A	Mercury	7439-97-6	0.00587	0.0833	mg/kg	71 - 137	0 - 14	85 - 121	0 - 10
EPA 6010B	Molybdenum	7439-98-7	0.132	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Nickel	7440-02-0	0.145	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Selenium	7782-49-2	0.300	0.750	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Silver	7440-22-4	0.0857	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Thallium	7440-28-0	0.152	0.750	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Vanadium	7440-62-2	0.141	0.250	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 6010B	Zinc	7440-66-6	0.178	1.00	mg/kg	75 - 125	0 - 20	80 - 120	0 - 20
EPA 7196A	Chromium VI	18540-29-9	0.22	0.80	mg/kg	75 - 125	0 - 25	80 - 120	0 - 20
EPA 8081A	Aldrin	309-00-2	1.5	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Chlordane	57-74-9	20	50	µg/kg	--	--	--	--
EPA 8081A	DDT/DDE/DDD	50-29-3	1.6	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Dieldrin	60-57-1	1.1	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Endrin	72-20-8	1.0	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Heptachlor (& its Epoxide)	76-44-8	1.1	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Kepone	143-50-0	0.75	5.0	µg/kg				
EPA 8081A	Lindane	58-89-9	1.1	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Methoxychlor	72-43-5	0.84	5.0	µg/kg	50 - 135	0 - 25	50 - 135	0 - 25
EPA 8081A	Mirex	2385-85-5	1.2	5.0	µg/kg	--	--	--	--
EPA 8081A	Toxaphene	8001-35-2	42	100	µg/kg	--	--	--	--
EPA 8151A	2,4-Dichlorophenoxyacetic acid	94-75-7	14	100	µg/kg	30 - 130	0 - 30	30 - 130	0 - 30
EPA 8151A	2,4,5-TP (Silvex)	93-72-1	2.3	10	µg/kg	30 - 150	0 - 30	30 - 150	0 - 30

Table 3b
Laboratory QC Control Limits (Soil)
Omega Superfund Site Operable Unit 2

METHOD	COMPOUND	CAS	MDL	RL	UNIT	MS CL	MS RPD	LCS CL	LCS RPD
EPA 8260B	1,1-Dichloroethene	75-35-4	0.35	5.0	µg/kg	47 - 143	0 - 25	74 - 122	0 - 20
EPA 8260B	1,2-Dichloroethane	107-06-2	0.31	5.0	µg/kg	70 - 130	0 - 20	70 - 130	0 - 20
EPA 8260B	1,4-Dichlorobenzene	106-46-7	0.22	5.0	µg/kg	70 - 130	0 - 20	70 - 130	0 - 20
EPA 8260B	2-Butanone	78-93-3	3.8	50	µg/kg	70 - 130	0 - 20	70 - 130	0 - 20
EPA 8260B	Benzene	71-43-2	0.13	5.0	µg/kg	61 - 127	0 - 20	78 - 120	0 - 20
EPA 8260B	Carbon Tetrachloride	56-23-5	0.28	5.0	µg/kg	51 - 135	0 - 29	49 - 139	0 - 20
EPA 8260B	Chlorobenzene	108-90-7	0.22	5.0	µg/kg	57 - 123	0 - 20	79 - 120	0 - 20
EPA 8260B	Chloroform	67-66-3	0.24	5.0	µg/kg	70 - 130	0 - 20	70 - 130	0 - 20
EPA 8260B	Tetrachloroethene	127-18-4	0.21	5.0	µg/kg	70 - 130	0 - 20	70 - 130	0 - 20
EPA 8260B	Trichloroethene	79-01-6	0.30	5.0	µg/kg	44 - 158	0 - 20	70 - 130	0 - 20
EPA 8260B	Vinyl Chloride	75-01-4	0.50	5.0	µg/kg	49 - 139	0 - 47	68 - 122	0 - 20
EPA 8270C	2-Methylphenol (o-cresol)	95-48-7	0.017	0.50	mg/kg	40 - 105	0 - 30	40 - 105	0 - 30
EPA 8270C	3/4-Methylphenol (m/p-cresol)	65794-96-9	0.033	0.50	mg/kg	40 - 105	0 - 30	40 - 105	0 - 30
EPA 8270C	2,4-Dinitrotoluene	121-14-2	0.013	0.50	mg/kg	50 - 115	0 - 30	50 - 115	0 - 30
EPA 8270C	Hexachlorobenzene	118-74-1	0.013	0.50	mg/kg	45 - 120	0 - 30	45 - 120	0 - 30
EPA 8270C	Hexachlorobutadiene	87-68-3	0.013	0.50	mg/kg	40 - 115	0 - 30	40 - 115	0 - 30
EPA 8270C	Hexachloroethane	67-72-1	0.016	0.50	mg/kg	35 - 110	0 - 30	35 - 110	0 - 30
EPA 8270C	Nitrobenzene	98-95-3	0.32	2.5	mg/kg	60 - 115	0 - 30	60 - 115	0 - 30
EPA 8270C	Pentachlorophenol	87-86-5	0.39	2.5	mg/kg	25 - 120	0 - 30	25 - 120	0 - 30
EPA 8270C	Pyridine	110-86-1	0.055	0.50	mg/kg	50 - 130	0 - 20	52 - 115	0 - 20
EPA 8270C	2,4,5-Trichlorophenol	95-95-4	0.013	0.50	mg/kg	50 - 100	0 - 30	50 - 100	0 - 30
EPA 8270C	2,4,6-Trichlorophenol	88-06-2	0.015	0.50	mg/kg	45 - 110	0 - 30	45 - 110	0 - 30
DHS LUFT	Organic Lead	--	0.209	1.00	mg/kg	22 - 148	0 - 18	72 - 126	0 - 30

Notes:
QC - quality control
µg/kg - micrograms per kilogram
mg/kg - milligrams per kilogram
pg/g - picograms per gram
CAS - Chemical Abstracts Service
EPA - Environmental Protection Agency
LCS CL - laboratory check sample control limit
LCS RPD - laboratory check sample relative percent difference
MDL - method detection limit
MS CL - matrix spike control limit
MS RPD - matrix spike relative percent difference
RL - reporting limit
TPH - total petroleum hydrocarbons

Table 4
Laboratory Control Tiers
Omega Superfund Site Operable Unit 2

The options available for data reporting from an analytical laboratory are presented in four general levels. The levels indicate the detail of reporting for the analyses, and the components included in the data package for each level are given below.
■**LEVEL IV :** All QC data included in Levels I, II, and III, multiple sample dilution reports, initial and continuing calibration chromatograms and quantitation reports, and standard preparation logs.
■**LEVEL III :** All QC data included in Levels I and II, MS/MSD analysis performed on specific sample upon request, chromatograms (including QC and samples), quantitation reports, initial and continuing calibration information, analysis logs, and extraction logs.
■**LEVEL II:** Analytical reports, chain of custody form, method blank, matrix spike/ spike duplicate summary with control limits, laboratory control samples with control limits, reporting limits listed on all reports, surrogate recoveries for GC and GC/MS analyses with control limits, case narrative upon request, and corrective action reports when necessary.
■**LEVEL I:** Analytical reports, chain of custody form, case narrative upon request, and corrective action reports when necessary.

Notes:
QC - quality control
MS - matrix spike
MSD - matrix spike duplicate
GC - gas chromatography
GC/MS - gas chromatography/mass spectrometry

Table 5a

Reporting Limits, Holding Times, Containers, Preservation

Work Area Monitoring and Leading Edge Investigation

Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[1] (µg/L)
EPA 8260B	Carbon Tetrachloride	0.5	14	40ml VOA Vial	0≤6° C, HCl, pH <2, no headspace	0.5
EPA 8260B	Chloroform	0.5	14	40ml VOA Vial		80*
EPA 8260B	1,1-Dichloroethane	0.5	14	40ml VOA Vial		5
EPA 8260B	1,2-Dichloroethane	0.5	14	40ml VOA Vial		0.5
EPA 8260B	c-1,2-Dichloroethene	0.5	14	40ml VOA Vial		6
EPA 8260B	1,1-Dichloroethene	0.5	14	40ml VOA Vial		6
EPA 8260B	Tetrachloroethene	0.5	14	40ml VOA Vial		5
EPA 8260B	1,1,1-Trichloroethane	0.5	14	40ml VOA Vial		200
EPA 8260B	Trichloroethene	0.5	14	40ml VOA Vial		5
EPA 8260B	Trichlorofluoromethane	0.5	14	40ml VOA Vial		150
EPA 8260B	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.5	14	40ml VOA Vial		1200
EPA 8270C SIM	1,4-Dioxane	1	7 days /40 days	1L Amber	0≤6° C	1**
EPA 218.6	Chromium VI	1	24 hrs[2]	250ml Poly	0≤6° C	10

Notes:

1 - California Drinking Water Standard Primary Maximum Contaminant Level

2 - If sample is field filtered and stored in ammonia sulfate buffer preservative above pH 9.3, 28-day hold times are permitted.

* - Total trihalomethanes = Bromodichloromethane, Bromoform, Chloroform, Dibromochloromethane

** - California State Notification Levels for Drinking Water

Reference:

California Code of Regulation Title 22. Table 64444-A. Last updated June 14, 2016

http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/dwregulations-2016-06-14.pdf

Drinking Water Notification Levels and Response Levels: An Overview. Division of Drinking Water State Water Resources Control Board. February 4, 2015

http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf

Acronyms:

°C - degree Celsius

COC - chemical of concern

HCl - hydrochloric acid

L - Liter

MCL - maximum containment level

ml - milliliter

µg/L - microgram per liter

SIM - selective ion monitoring

VOA - volatile organic analysis

Table 5b
Reporting Limits, Holding Times, Containers, Preservation
Pre-Design Investigation
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	Main COCs	COPCs	Standards for End-Use	Key Treatment for Constituents	Waste Discharge Requirement[1]	Water Quality Objectives[2]	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[3] (µg/L)	Minimum Levels[4] (µg/L)
EPA 200.7	Aluminum		X					50	6 months	250ml Poly	HNO_3 pH<2	1000	
EPA 200.7 EPA 200.8[6]	Antimony		X			X		15 1				6	5
EPA 200.7 EPA 200.8[6]	Arsenic		X			X		15 1				10	10
EPA 200.7 EPA 1640[6]	Beryllium					X		10 0.5					0.5
EPA 200.7	Boron						X	20					
EPA 200.7 EPA 1640[6]	Cadmium					X		10 0.03					0.5
EPA 200.7	Chromium (Total)		X		X	X		10				50	10 (III)
EPA 200.7 EPA 1640[6]	Copper					X		10 0.03					0.5
EPA 200.7 EPA 1640[6]	Lead					X		10 0.03					0.5
EPA 200.7	Manganese		X		X			5				50***	
EPA 200.7 EPA 200.8[6]	Nickel		X			X		10 1				100	1
EPA 200.7 EPA 200.8[6]	Selenium		X			X		15 1				50	2
EPA 200.7 EPA 1640[6]	Silver					X		5 0.05					0.25
EPA 200.7 EPA 200.8[6]	Thallium		X			X		15 1				2	1
EPA 200.7	Vanadium		X					10				50**	
EPA 200.7	Zinc					X		10					20
EPA 218.6	Chromium VI	X	X			X		1	24 hrs[5]	250ml Poly	0≤6° C	10	5
EPA 245.1	Mercury		X			X		0.2	28	250ml Poly	HNO_3 pH<2	2	0.2
EPA 300.0	Chloride						X	1 (mg/L)	28	125ml Poly	0≤6° C		
EPA 300.0	Nitrate (as N)				X			0.1 (mg/L)	48 hrs				
EPA 300.0	Sulfate				X		X	1 (mg/L)	28				
EPA 314.0	Perchlorate		X		X	X		2	28	125ml Poly	0≤6° C	6	6†
EPA 504.1	1,2-Dibromo-3-chloropropane (DBCP)		X					0.01	14	40ml VOA Vial	0≤6° C, $Na_2S_2O_3$	0.2	
EPA 504.1	1,2-Dibromoethane (Ethylene Dibromide - EDB)		X			X		0.01				0.05	0.05†
SRL 524M-TCP	1,2,3-Trichloropropane		X					0.005	14	40ml VOA Vial	0≤6° C, HCl, pH <2 no headspace	0.005**	
EPA 1625M	n-Nitrosodimethylamine (NDMA)		X			X		0.01	7 / 40	2 x 1L Amber	0≤6° C	0.01**	5
SM 2540 C	Solids, Total Dissolved		X		X		X	1 (mg/L)	7	1L Poly	0≤6° C	500 (mg/L)***	
SM 4500 CN E	Cyanide					X		0.02 (mg/L)	14	1L Poly	0≤6° C, NaOH, pH>10		5
EPA 8015B (M)	Methanol					X		0.1 (mg/L)	14	40ml VOA Vial	0≤6° C, no headspace		1000
EPA 8015B (M)	Total Petroleum Hydrocarbons					X		100	7 / 40	500ml Amber	0≤6° C		0

Table 5b
Reporting Limits, Holding Times, Containers, Preservation
Pre-Design Investigation
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	Main COCs	COPCs	Standards for End-Use	Key Treatment for Constituents	Waste Discharge Requirement[1]	Water Quality Objectives[2]	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[3] (µg/L)	Minimum Levels[4] (µg/L)
EPA 8081A	4,4'-DDD					X		0.05	7 / 40	2 x 1L Amber	0≤6° C		0.05
EPA 8081A	4,4'-DDE					X		0.05					0.05
EPA 8081A EPA 608[6]	4,4'-DDT					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	Alpha-Endosulfan					X		0.05 0.004					0.02
EPA 8081A EPA 608[6]	Alpha-BHC					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	Aldrin					X		0.05 0.004					0.005
EPA 8081A EPA 608[6]	Beta-Endosulfan					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	beta-BHC					X		0.05 0.005					0.005
EPA 8081A EPA 608[6]	Chlordane					X		0.5 0.05					0.1
EPA 8081A EPA 608[6]	delta-BHC					X		0.05 0.004					0.005
EPA 8081A EPA 608[6]	Dieldrin					X		0.05 0.004					0.01
EPA 8081A	Endosulfan Sulfate					X		0.05					0.05
EPA 8081A EPA 608[6]	Endrin					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	Endrin Aldehyde					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	Heptachlor					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	Heptachlor Epoxide					X		0.05 0.004					0.01
EPA 8081A EPA 608[6]	gamma-BHC					X		0.05 0.004					0.02
EPA 8081A EPA 608[6]	Toxaphene					X		2 0.3					0.5
EPA 8082	PCB 1016					X		0.5	7 / 40	2 x 1L Amber	0≤6° C		0.5
EPA 8082	PCB 1221					X		0.5					0.5
EPA 8082	PCB 1232					X		0.5					0.5
EPA 8082	PCB 1242					X		0.5					0.5
EPA 8082	PCB 1248					X		0.5					0.5
EPA 8082	PCB 1254					X		0.5					0.5
EPA 8082	PCB 1260					X		0.5					0.5
EPA 8260B	1,1,1-Trichloroethane	X	X			X		0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	200	2
EPA 8260B	1,1,2,2-Tetrachloroethane		X			X		0.5	14	40ml VOA Vial, no headspace		1	0.5
EPA 8260B	1,1,2-Trichloro-1,2,2-Trifluoroethane	X	X					0.5	14	40ml VOA Vial, no headspace		1200	
EPA 8260B	1,1,2-Trichloroethane		X	X		X		0.5	14	40ml VOA Vial, no headspace		5	0.5
EPA 8260B	1,1-Dichloroethane	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		5	1
EPA 8260B	1,1-Dichloroethene	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		6	0.5
EPA 8260B	1,2,4-Trichlorobenzene					X		0.5	14	40ml VOA Vial, no headspace			5
EPA 8260B	1,2-Dichlorobenzene					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	1,2-Dichloroethane	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		0.5	0.5
EPA 8260B	1,2-Dichloropropane					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	1,3-Dichloropropane		X					1	14	40ml VOA Vial, no headspace			
EPA 8260B	1,3-Dichlorobenzene					X		0.5	14	40ml VOA Vial, no headspace			2
EPA 8260B	1,4-Dichlorobenzene					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	2-Butanone (methyl ethyl ketone)					X		5	14	40ml VOA Vial, no headspace			700†

Table 5b
Reporting Limits, Holding Times, Containers, Preservation
Pre-Design Investigation
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	Main COCs	COPCs	Standards for End-Use	Key Treatment for Constituents	Waste Discharge Requirement[1]	Water Quality Objectives[2]	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[3] (µg/L)	Minimum Levels[4] (µg/L)
EPA 8260B EPA 524.2[6]	2-Chloroethyl Vinyl Ether					X		5 1	7	40ml VOA Vial, no headspace	0≤6° C		1
EPA 8260B	Acetone					X		10	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2		700†
EPA 8260B EPA 624[6]	Acrolein					X		20 5	14	40ml VOA Vial, no headspace			5
EPA 8260B EPA 524.2[6]	Acrylonitrile					X		10 2	14	40ml VOA Vial, no headspace			2
EPA 8260B	Benzene		X			X		0.5	14	40ml VOA Vial, no headspace		1	0.5
EPA 8260B	Bromodichloromethane					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	Bromoform					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	Bromomethane (Methyl Bromide)					X		1	14	40ml VOA Vial, no headspace			2
EPA 8260B	c-1,2-Dichloroethene	X	X	X				0.5	14	40ml VOA Vial, no headspace		6	
EPA 8260B	c-1,3-Dichloropropene					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	Carbon Disulfide		X					1	14	40ml VOA Vial, no headspace		160**	
EPA 8260B	Carbon Tetrachloride	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		0.5	0.5
EPA 8260B	Chlorobenzene		X			X		0.5	14	40ml VOA Vial, no headspace		70	2
EPA 8260B	Chloroethane					X		0.5	14	40ml VOA Vial, no headspace			2
EPA 8260B	Chloroform	X	X			X		0.5	14	40ml VOA Vial, no headspace		80*	2
EPA 8260B	Chloromethane (Methyl Chloride)					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	Dibromochloromethane					X		0.5	14	40ml VOA Vial, no headspace			0.5
EPA 8260B	Diisopropyl Ether (DIPE)					X		0.5	14	40ml VOA Vial, no headspace			2
EPA 8260B	Ethanol					X		50	14	40ml VOA Vial, no headspace			1000
EPA 8260B	Ethylbenzene					X		0.5	14	40ml VOA Vial, no headspace		300	2
EPA 8260B	Ethyl-t-Butyl Ether (ETBE)					X		0.5	14	40ml VOA Vial, no headspace			2
EPA 8260B EPA 524.2[6]	Methylene Chloride (Dichloromethane)					X		1 0.5	14	40ml VOA Vial, no headspace		5	0.5
EPA 8260B	Methyl-t-Butyl Ether (MTBE)		X			X		0.5	14	40ml VOA Vial, no headspace		13	5†
EPA 8260B	Naphthalene					X		1	14	40ml VOA Vial, no headspace			10
EPA 8260B	o-Xylene					X		0.5	14	40ml VOA Vial, no headspace			1750†
EPA 8260B	p/m-Xylene					X		0.5	14	40ml VOA Vial, no headspace			1750†
EPA 8260B	t-1,2-Dichloroethene		X			X		0.5	14	40ml VOA Vial, no headspace		6	1
EPA 8260B	t-1,3-Dichloropropene		X			X		0.5	14	40ml VOA Vial, no headspace		0.5*	0.5
EPA 8260B	Tert-Amyl-Methyl Ether (TAME)					X		0.5	14	40ml VOA Vial, no headspace			2
EPA 8260B	Tert-Butyl Alcohol (TBA)					X		10	14	40ml VOA Vial, no headspace			10
EPA 8260B	Tetrachloroethene	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		5	0.5
EPA 8260B	Toluene		X			X		0.5	14	40ml VOA Vial, no headspace		150	2
EPA 8260B	Trichloroethene	X	X	X		X		0.5	14	40ml VOA Vial, no headspace		5	0.5
EPA 8260B	Trichlorofluoromethane	X	X					0.5	14	40ml VOA Vial, no headspace		150	
EPA 8260B	Vinyl Chloride		X			X		0.5	14	40ml VOA Vial, no headspace		0.5	0.5
EPA 8270C EPA 625[6]	1,2-Diphenylhydrazine-(as-Azobenzene)					X		10 0.5	7 / 40	1L Amber	0≤6° C		1
EPA 8270C EPA 625[6]	2-Chlorophenol					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	2,4-Dichlorophenol					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	2,4-Dimethylphenol					X		10 1	7 / 40	1L Amber			2
EPA 8270C EPA 625[6]	2,4-Dinitrophenol					X		50 5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	2,4-Dinitrotoluene					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C	2,4,6-Trichlorophenol					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	2,6-Dinitrotoluene					X		10 5	7 / 40	1L Amber			5
EPA 8270C	2-Nitrophenol					X		10	7 / 40	1L Amber			10
EPA 8270C	2-Chloronaphthalene					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	3,3'-Dichlorobenzidine					X		25 5	7 / 40	1L Amber			5

Table 5b
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METHOD	ANALYTE	Main COCs	COPCs	Standards for End-Use	Key Treatment for Constituents	Waste Discharge Requirement[1]	Water Quality Objectives[2]	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[3] (µg/L)	Minimum Levels[4] (µg/L)
EPA 8270C EPA 625[6]	3-Methyl-4-Chlorophenol					X		10 0.5	7 / 40	1L Amber			1
EPA 8270C EPA 625[6]	2-Methyl-4,6-Dinitrophenol					X		50 5	7 / 40	1L Amber			5
EPA 8270C EPA 625 SIM[6]	4-Nitrophenol					X		10 5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	4-Bromophenyl-phenyl-ether					X		10 5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	4-Chlorophenyl-phenyl-ether					X		10 5	7 / 40	1L Amber			5
EPA 8270C EPA 625 SIM[6]	Acenaphthene					X		10 0.2	7 / 40	1L Amber			1
EPA 8270C	Acenaphthylene					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Anthracene					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	Benzidine					X		50 5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	Benzo (a) Anthracene					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	Benzo (a) Pyrene					X		10 0.5	7 / 40	1L Amber			2
EPA 8270C	Benzo (b) Fluoranthene					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Benzo (g,h,i) Perylene					X		10 1	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	Benzo (k) Fluoranthene					X		10 1	7 / 40	1L Amber			2
EPA 8270C EPA 625[6]	Bis (2-Chloroethoxyl) methane					X		10 0.5	7 / 40	1L Amber	0≤6° C		5
EPA 8270C EPA 625[6]	Bis (2-Chloroethyl) ether					X		25 0.5	7 / 40	1L Amber			1
EPA 8270C	Bis (2-Chloroisopropyl) ether					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Bis (2-Ethylhexyl) Phthalate		X		X	X		10 5[7]	7 / 40	1L Amber		4	5
EPA 8270C	Butyl benzyl phthalate					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Chrysene					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625 SIM[6]	Dibenzo(a,h)-anthracene					X		10 0.2[7]	7 / 40	1L Amber			0.1
EPA 8270C	Diethyl phthalate					X		10	7 / 40	1L Amber			10
EPA 8270C	Dimethyl phthalate					X		10	7 / 40	1L Amber			10
EPA 8270C	di-n-Butyl phthalate					X		10	7 / 40	1L Amber			10
EPA 8270C	di-n-Octyl phthalate					X		10	7 / 40	1L Amber			10
EPA 8270C	Fluoranthene					X		10	7 / 40	1L Amber			10
EPA 8270C	Fluorene					X		10	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Hexachlorobenzene					X		10 0.5	7 / 40	1L Amber			1
EPA 8270C EPA 625[6]	Hexachlorobutadiene					X		10 1	7 / 40	1L Amber			1
EPA 8270C EPA 625[6]	Hexachloro-cyclopentadiene					X		25 0.5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	Hexachloroethane					X		10 1	7 / 40	1L Amber			1
EPA 8270C EPA 625 SIM[6]	Indeno(1,2,3,cd)-pyrene					X		10 0.2[7]	7 / 40	1L Amber			0.05

Table 5b
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METHOD	ANALYTE	Main COCs	COPCs	Standards for End-Use	Key Treatment for Constituents	Waste Discharge Requirement[1]	Water Quality Objectives[2]	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	California MCL[3] (µg/L)	Minimum Levels[4] (µg/L)
EPA 8270C EPA 625[6]	Isophorone					X		10 0.5	7 / 40	1L Amber	0≤6° C		1
EPA 8270C EPA 625[6]	N-Nitroso-di-n-propyl amine					X		10 5	7 / 40	1L Amber			5
EPA 8270C EPA 625[6]	N-Nitrosodiphenyl amine					X		10 0.5	7 / 40	1L Amber			1
EPA 8270C EPA 625[6]	Nitrobenzene					X		25 1	7 / 40	1L Amber			10
EPA 8270C EPA 625[6]	Pentachlorophenol					X		10 0.5	7 / 40	1L Amber			1
EPA 8270C EPA 625[6]	Phenanthrene					X		10 0.5	7 / 40	1L Amber			5
EPA 8270C	Phenol					X		10	7 / 40	1L Amber			50
EPA 8270C	Pyrene					X		10	7 / 40	1L Amber			10
EPA 8270C SIM	1,4-Dioxane	X	X			X		1	7 / 40	1L Amber	0≤6° C	1**	3†
EPA 1613	Dioxin (2,3,7,8-TCDD)					X		0.000005	365	Amber Glass	0≤6° C		1.00E-05
EPA 100.2	Asbestos					X		0.2MFL	48 hrs	1 liter polyethylene or glass container; should be collected in duplicate. 800 mls in 1 liter bottles and stored in the dark at 4.0 degrees C. sample are to be shipped in order to be filtered at the laboratory within 48 hrs.	none		7,000,000† (in fibers/L k,s.)

Notes:
1 - List of pollutant to be screened under ORDER NO. R4-2013-0095
2 - List of pollutant to be screened under the Basin Plan
3 - California Drinking Water Standard Primary Maximum Contaminant Level for COCs and COPCs
4 - Minimum Levels under Order NO. R4-2013-0095
5 - If sample is field filtered and stored in ammonia sulfate buffer preservative above pH 9.3, 28-day hold times are permitted.
6 - Second analytical method and reporting limit reflects a drinking water method that may be subsituted to meet MCLs or minimum detection levels for project.
7 - MCL or minimum detection limit for these 3 SVOC analytes is between the analytical method reporting limit and the method detection limit for the listed drinking water method.

* - Total trihalomethanes = Bromodichloromethane, Bromoform, Chloroform, Dibromochloromethane
* - Total 1,3-Dichloropropene = c-1,3-Dichloropropene and t-1,3-Dichloropropene
** - California State Notification Levels for Drinking Water
*** - California Drinking Water Standard Secondary Maximum Contaminant Level
† - Screening level that applies to non-MUN receiving waters under ORDER NO. R4-2013-0095

Acronyms:
°C - degree Celsius
COC - chemical of concern
COPC - chemical of potential concern
DLR - detection limit for purposes of reporting
EPA - Environmental Protection Agency
HCl - hydrochloric acid
HNO_3 - nitric acid
L - Liter
MCL - maximum containment level
MFL - million fibers per liter
mL - milligram per liter
NaOH - sodium hydroxide
PHG - public health goal
TPH - total petroleum hydrocarbon
µg/L - microgram per liter
VOA - volatile organic acid

Reference:
California Code of Regulation Title 22. Sections 64431, 64444, 64449, and 64533. Last updated June 14, 2016
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/dwregulations-2016-06-14.pdf
Drinking Water Notification Levels and Response Levels: An Overview. Division of Drinking Water State Water Resources Control Board. February 4, 2015
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf

Los Angeles Regional Water Quality Control Board, Order NO. R4-2013-0095, General NPDES Permit NO. CAG994004, Waste Discharge Requirements from Construction and Project Dewatering to Surface Waters in Coastal Watersheds of Los Angeles and Ventura Counties - Attachment B and E

http://www.waterboards.ca.gov/losangeles/board_decisions/adopted_orders/permits/general/npdes/r4-2013-0095
Los Angeles Regional Water Quality Control Board, Basin Plan for the Coastal Watersheds of Los Angeles and Ventura Counties, Table 3-13, 2 May 2013
http://www.waterboards.ca.gov/losangeles/water_issues/programs/basin_plan

Table 5c
Reporting Limits, Holding Times, Containers, Preservation
Water-Investigation Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 100.2	Asbestos	0.2MFL	48 hrs	1 liter polyethylene or glass container; should be collected in duplicate. 800 mls in 1 liter bottles and stored in the dark at 4.0 degrees C. sample are to be shipped in order to be filtered at the laboratory within 48 hrs.	none	--	--	1%
EPA 200.7	Antimony	15	6 months	250ml Poly	HNO_3, pH<2	--	15	500
EPA 200.7	Arsenic	15	6 months	250ml Poly	HNO_3, pH<2	5.0	5.0	500
EPA 200.7	Barium	10	6 months	250ml Poly	HNO_3, pH<2	100	100	10,000[2]
EPA 200.7	Beryllium	10	6 months	250ml Poly	HNO_3, pH<2	--	0.75	75
EPA 200.7	Cadmium	10	6 months	250ml Poly	HNO_3, pH<2	1.0	1.000	100
EPA 200.7	Chromium	10	6 months	250ml Poly	HNO_3, pH<2	5	5 (560)	2,500
EPA 200.7	Cobalt	10	6 months	250ml Poly	HNO_3, pH<2	--	80	8,000
EPA 200.7	Copper	10	6 months	250ml Poly	HNO_3, pH<2	--	25	2,500
EPA 200.7	Lead	10	6 months	250ml Poly	HNO_3, pH<2	5.0	5.0	1,000
EPA 245.1	Mercury	0.2	28	250ml Poly	HNO_3, pH<2	0.2	0.2	20
EPA 200.7	Molybdenum	10	6 months	250ml Poly	HNO_3, pH<2	--	350	3,500
EPA 200.7	Nickel	10	6 months	250ml Poly	HNO_3, pH<2	--	20	2,000
EPA 200.7	Selenium	15	6 months	250ml Poly	HNO_3, pH<2	1.0	1.0	100
EPA 200.7	Silver	5	6 months	250ml Poly	HNO_3, pH<2	5.0	5.0	500
EPA 200.7	Thallium	15	6 months	250ml Poly	HNO_3, pH<2	--	7.0	700
EPA 200.7	Vanadium	10	6 months	250ml Poly	HNO_3, pH<2	--	24	2,400
EPA 200.7	Zinc	10	6 months	250ml Poly	HNO_3, pH<2	--	250	5,000
EPA 218.6	Chromium VI	1	24 hrs[4]	250ml Poly	0≤6° C	--	5	500
EPA 300.0	Fluoride	100	28	125ml Poly	0≤6° C	--	180[c]	18,000[3]
EPA 1613	Dioxin (2,3,7,8-TCDD)	0.000005	365	Amber Glass	0≤6° C	--	0.001	0.01

Table 5c
Reporting Limits, Holding Times, Containers, Preservation
Water-Investigation Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 8015B (M)	Total Petroleum Hydrocarbons	100	7 days /40 days	500ml Amber	0≤6° C	--	--	--
EPA 8015B (M)	Gasoline	100	14	40ml VOA Vial	0≤6° C, HCl, pH <2	--	--	--
EPA 8015B (M)	Diesel	100	7 days /40 days	500ml Amber	0≤6° C	--	--	--
EPA 8015B (M)	Jet fuel	100	7 days /40 days	500ml Amber	0≤6° C	--	--	--
EPA 8151A	2,4-Dichlorophenoxyacetic acid	5	7 days /40 days	1L Amber	0≤6° C	10.0	10	100
EPA 8151A	2,4,5-TP (Silvex)	0.5	7 days /40 days	1L Amber	0≤6° C	1.0	1.0	10
EPA 8081A	Aldrin	0.05	7 days /40 days	1L Amber	0≤6° C	--	0.14	1.4
EPA 8081A	Chlordane	0.05	7 days /40 days	1L Amber	0≤6° C	0.03	0.25	2.5
EPA 8081A	DDT/DDE/DDD	0.05	7 days /40 days	1L Amber	0≤6° C	--	0.1	1.0
EPA 8081A	Dieldrin	0.05	7 days /40 days	1L Amber	0≤6° C	--	0.8	8.0
EPA 8081A	Endrin	0.05	7 days /40 days	1L Amber	0≤6° C	0.02	0.02	0.2
EPA 8081A	Heptachlor (& its Epoxide)	0.05	7 days /40 days	1L Amber	0≤6° C	0.008	0.47	4.7
EPA 8081A	Kepone	0.1	7 days /40 days	1L Amber	0≤6° C	--	2.1	21
EPA 8081A	Lindane	0.05	7 days /40 days	1L Amber	0≤6° C	0.4	0.4	4.0
EPA 8081A	Methoxychlor	0.05	7 days /40 days	1L Amber	0≤6° C	10.0	10	100
EPA 8081A	Mirex	0.1	7 days /40 days	1L Amber	0≤6° C	--	2.1	21
EPA 8081A	Toxaphene	2	7 days /40 days	1L Amber	0≤6° C	0.5	0.5	5.0
EPA 8260B	1,1-Dichloroethene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.7	--	--
EPA 8260B	1,2-Dichloroethane	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.5	--	--
EPA 8260B	1,4-Dichlorobenzene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	7.5	--	--
EPA 8260B	2-Butanone	5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	200.0	--	--
EPA 8260B	Benzene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.5	--	--
EPA 8260B	Carbon Tetrachloride	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.5	--	--
EPA 8260B	Chlorobenzene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	100.0	--	--
EPA 8260B	Chloroform	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	6.0	--	--
EPA 8260B	Tetrachloroethene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.7	--	--
EPA 8260B	Trichloroethene	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.5	204	2,040

Table 5c
Reporting Limits, Holding Times, Containers, Preservation
Water-Investigation Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/L)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 8260B	Vinyl Chloride	0.5	14	40ml VOA Vial, no headspace	0≤6° C, HCl, pH <2	0.2	--	--
EPA 8270C	2-Methylphenol (o-cresol)	10	7 days /40 days	1L Amber	0≤6° C	200.0	--	--
EPA 8270C	3/4-Methylphenol (m/p-cresol)	10	7 days /40 days	1L Amber	0≤6° C	200.0	--	--
EPA 8270C	Cresols (total)	10	7 days /40 days	1L Amber	0≤6° C	200.0	--	--
EPA 8270C	2,4-Dinitrotoluene	10	7 days /40 days	1L Amber	0≤6° C	0.13	--	--
EPA 8270C	Hexachlorobenzene	10	7 days /40 days	1L Amber	0≤6° C	0.13	--	--
EPA 8270C	Hexachlorobutadiene	10	7 days /40 days	1L Amber	0≤6° C	0.5	--	--
EPA 8270C	Hexachloroethane	10	7 days /40 days	1L Amber	0≤6° C	3.0	--	--
EPA 8270C	Nitrobenzene	25	7 days /40 days	1L Amber	0≤6° C	2.0	--	--
EPA 8270C	Pentachlorophenol	10	7 days /40 days	1L Amber	0≤6° C	100.0	1.7	17
EPA 8270C	Pyridine	10	7 days /40 days	1L Amber	0≤6° C	5.0	--	--
EPA 8270C	2,4,5-Trichlorophenol	10	7 days /40 days	1L Amber	0≤6° C	400.0	--	--
EPA 8270C	2,4,6-Trichlorophenol	10	7 days /40 days	1L Amber	0≤6° C	2.0	--	--
DHS LUFT	Organic Lead	300	7	500ml Amber	0≤6° C	--	--	13

Notes:

Constituents as presented in California Code of Regulations, Title 22, Section 66261.24.

1. Values expressed as net weight
2. Excluding barium sulfate
3. Limits given for fluoride salts
4. If sample is field filtered and stored in ammonia sulfate buffer preservative above pH 9.3, 28-day hold times are permitted.

mg/kg - milligrams per kilogram
mg/L - milligrams per liter
µg/L - micrograms per liter
° C - degrees celsius
EPA - United States Environmental Protection Agency
HCL - hydrochloric acid
HNO3 - nitric acid
hrs - hours
MFL - million fibers per liter
STLC - Soluble Threshold Limit Concentration
TCLP - Toxicity Characteristic Leaching Procedure
TTLC - Total Threshold Limit Concentration

Table 5d
Reporting Limits, Holding Times, Containers, Preservation
Soil Investigation-Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/kg)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 300.0	Fluoride	1 (mg/kg)	28	4oz. Jar	0≤6° C	--	180[c]	18,000[2]
EPA/600/R-93/116	Asbestos	<1.0%	6 months	4oz. Jar	0≤6° C	--	--	1%
EPA 1613	Dioxin (2,3,7,8-TCDD)	0.0005	365	4oz. Jar	0≤6° C	--	0.001	0.01
EPA 6010B	Antimony	0.75 (mg/kg)	6 months	4oz. Jar	0≤6° C	--	15	500
EPA 6010B	Arsenic	0.75 (mg/kg)	6 months	4oz. Jar		5.0	5.0	500
EPA 6010B	Barium	0.5 (mg/kg)	6 months	4oz. Jar		100	100	10,000[3]
EPA 6010B	Beryllium	0.25 (mg/kg)	6 months	4oz. Jar		--	0.75	75
EPA 6010B	Cadmium	0.5 (mg/kg)	6 months	4oz. Jar		1.0	1.000	100
EPA 6010B	Chromium	0.25 (mg/kg)	6 months	4oz. Jar		5	5 (560)	2,500
EPA 6010B	Cobalt	0.25 (mg/kg)	6 months	4oz. Jar		--	80	8,000
EPA 6010B	Copper	0.5 (mg/kg)	6 months	4oz. Jar		--	25	2,500
EPA 6010B	Lead	0.5 (mg/kg)	6 months	4oz. Jar		5.0	5.0	1,000
EPA 7471A	Mercury	0.0833 (mg/kg)	28	4oz. Jar		0.2	0.2	20
EPA 6010B	Molybdenum	0.25 (mg/kg)	6 months	4oz. Jar		--	350	3,500
EPA 6010B	Nickel	0.25 (mg/kg)	6 months	4oz. Jar		--	20	2,000
EPA 6010B	Selenium	0.75 (mg/kg)	6 months	4oz. Jar		1.0	1.0	100
EPA 6010B	Silver	0.25 (mg/kg)	6 months	4oz. Jar		5.0	5.0	500
EPA 6010B	Thallium	0.75 (mg/kg)	6 months	4oz. Jar		--	7.0	700
EPA 6010B	Vanadium	0.25 (mg/kg)	6 months	4oz. Jar		--	24	2,400
EPA 6010B	Zinc	1 (mg/kg)	6 months	4oz. Jar		--	250	5,000
EPA 7196A	Chromium VI	0.8 (mg/kg)	28	4oz. Jar	0≤6° C	--	5	500
EPA 8015B (M)	Total hydrocarbons	5 (mg/kg)	14	4oz. Jar	0≤6° C	--	--	--
EPA 8015B (M)	TPH as Gasoline	0.5 (mg/kg)	14	4oz. Jar		--	--	--
EPA 8015B (M)	TPH as Diesel	5 (mg/kg)	14	4oz. Jar		--	--	--
EPA 8081A	Aldrin	5	14 days /40 days	4oz. Jar	0≤6° C	--	0.14	1.4
EPA 8081A	Chlordane	50	14 days /40 days	4oz. Jar	0≤6° C	0.03	0.25	2.5
EPA 8081A	DDT/DDE/DDD	5	14 days /40 days	4oz. Jar	0≤6° C	--	0.1	1.0
EPA 8081A	Dieldrin	5	14 days /40 days	4oz. Jar	0≤6° C	--	0.8	8.0
EPA 8081A	Endrin	5	14 days /40 days	4oz. Jar	0≤6° C	0.02	0.02	0.2
EPA 8081A	Heptachlor (& its Epoxide)	10	14 days /40 days	4oz. Jar	0≤6° C	0.008	0.47	4.7
EPA 8081A	Kepone	5	14 days /40 days	4oz. Jar	0≤6° C	--	2.1	21

Table 5d
Reporting Limits, Holding Times, Containers, Preservation
Soil Investigation-Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/kg)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 8081A	Lindane	5	14 days /40 days	4oz. Jar	0≤6° C	0.4	0.4	4.0
EPA 8081A	Methoxychlor	5	14 days /40 days	4oz. Jar	0≤6° C	10.0	10	100
EPA 8081A	Mirex	5	14 days /40 days	4oz. Jar	0≤6° C	--	2.1	21
EPA 8081A	Toxaphene	100	14 days /40 days	4oz. Jar	0≤6° C	0.5	0.5	5.0
EPA 8151A	2,4-Dichlorophenoxyacetic acid	100	14 days /40 days	4oz. Jar	0≤6° C	10.0	10	100
EPA 8151A	2,4,5-TP (Silvex)	10	14 days /40 days	4oz. Jar	0≤6° C	1.0	1.0	10
EPA 8260B	1,1-Dichloroethene	5	14	4oz. Jar no headspace	0≤6° C	0.7	--	--
EPA 8260B	1,2-Dichloroethane	5	14	4oz. Jar no headspace	0≤6° C	0.5	--	--
EPA 8260B	1,4-Dichlorobenzene	5	14	4oz. Jar no headspace	0≤6° C	7.5	--	--
EPA 8260B	2-Butanone	50	14	4oz. Jar no headspace	0≤6° C	200.0	--	--
EPA 8260B	Benzene	5	14	4oz. Jar no headspace	0≤6° C	0.5	--	--
EPA 8260B	Carbon Tetrachloride	5	14	4oz. Jar no headspace	0≤6° C	0.5	--	--
EPA 8260B	Chlorobenzene	5	14	4oz. Jar no headspace	0≤6° C	100.0	--	--
EPA 8260B	Chloroform	5	14	4oz. Jar no headspace	0≤6° C	6.0	--	--
EPA 8260B	Tetrachloroethene	5	14	4oz. Jar no headspace	0≤6° C	0.7	--	--
EPA 8260B	Trichloroethene	5	14	4oz. Jar no headspace	0≤6° C	0.5	204	2,040
EPA 8260B	Vinyl Chloride	5	14	4oz. Jar no headspace	0≤6° C	0.2	--	--
EPA 8270C	2-Methylphenol (o-cresol)	500	14 days /40 days	4oz. Jar	0≤6° C	200.0	--	--
EPA 8270C	3/4-Methylphenol (m/p-cresol)	500	14 days /40 days	4oz. Jar	0≤6° C	200.0	--	--
EPA 8270C	Cresols (total)	500	14 days /40 days	4oz. Jar	0≤6° C	200.0	--	--
EPA 8270C	2,4-Dinitrotoluene	500	14 days /40 days	4oz. Jar	0≤6° C	0.13	--	--
EPA 8270C	Hexachlorobenzene	500	14 days /40 days	4oz. Jar	0≤6° C	0.13	--	--
EPA 8270C	Hexachlorobutadiene	500	14 days /40 days	4oz. Jar	0≤6° C	0.5	--	--
EPA 8270C	Hexachloroethane	500	14 days /40 days	4oz. Jar	0≤6° C	3.0	--	--
EPA 8270C	Nitrobenzene	2500	14 days /40 days	4oz. Jar	0≤6° C	2.0	--	--
EPA 8270C	Pentachlorophenol	2500	14 days /40 days	4oz. Jar	0≤6° C	100.0	1.7	17
EPA 8270C	Pyridine	500	14 days /40 days	4oz. Jar	0≤6° C	5.0	--	--
EPA 8270C	2,4,5-Trichlorophenol	500	14 days /40 days	4oz. Jar	0≤6° C	400.0	--	--

Table 5d
Reporting Limits, Holding Times, Containers, Preservation
Soil Investigation-Derived Waste
Omega Superfund Site Operable Unit 2

METHOD	ANALYTE	REPORTING LIMIT (µg/kg)	HOLDING TIME (days)	CONTAINER	PRESERVATION	TCLP (mg/L)	STLC (mg/L)	TTLC[1] (mg/kg)
EPA 8270C	2,4,6-Trichlorophenol	500	14 days /40 days	4oz. Jar	0≤6° C	2.0	--	--
DHS LUFT	Organic Lead Compounds	1 (mg/kg)	14	4oz. Jar	0≤6° C	--	--	13

Notes:

Constituents as presented in California Code of Regulations, Title 22, Section 66261.24.

1. Values expressed as net weight
2. Limits given for fluoride salts
3. Excluding barium sulfate

-- - not applicable

mg/kg - milligrams per kilogram
mg/L - milligrams per liter
µg/kg - micrograms per kilogram
EPA - United States Environmental Protection Agency
oz - ounces
STLC - Soluble Threshold Limit Concentration
TCLP - Toxicity Characteristic Leaching Procedure
TTLC - Total Threshold Limit Concentration
° C - degrees celsius

Table 6
Field Sample QC Frequency
Omega Superfund Site Operable Unit 2

Parameter	Trip Blanks	MS/MSD[1]	Equipment Rinsate Blanks[2]	Field Blank	Duplicate Samples
VOCs	1 per cooler of VOC samples	1 set/20 samples	1 per 10 samples or 1 per day	1 per source or 1 per day	1 per 10 samples (10%)
SVOCs	NA	1 set/20 samples	1 per 10 samples or 1 per day	NA	1 per 10 samples (10%)
Metals	NA	1 set/20 samples	1 per 10 samples or 1 per day	1 per source or 1 per day	1 per 10 samples (10%)
Asbestos	NA	NA	1 per 10 samples or 1 per day	NA	1 per 10 samples (10%)
Cyanide, Dioxin, Inorganic compounds, NDMA, PCBs, Pesticides, 1,2,3-TCP, and TPH compounds	NA	1 set/20 samples	1 per 10 samples or 1 per day	NA	1 per 10 samples (10%)

Notes:
1. Field personnel must collect triple volume to account for MS/MSD sample.
2. No equipment blanks are required for disposable or dedicated field sampling equipment.

NA - Not Applicable
VOC - Volatile Organic Compound
SVOC - Semi-Volatile Organic Compound
MS/MSD - Matrix Spike/Matrix Spike Duplicate
PCB - Polychlorinated Biphenyl

Table 7
Laboratory QC Requirements
Omega Superfund Site Operable Unit 2

	100.2	200.7	200.8	218.6	245.1	300	314	504.1	524	SRL 524 (M)	608
Initial Calibration (Minimum No. of pts.)	N/A	2	2	5	5	5	5	5	5	5	5
Initial Calibration Acceptance Criteria	95% Conformance	No acceptance criteria unless more than one standard is used, in which case $R \geq 0.995$	No acceptance criteria unless more than one standard is used, in which case $R \geq 0.995$	Linear least squares regression $R \geq 0.999$, or non-linear – COD r2 $\geq$ 0.998 (minimum of 6 points)	$R \geq 0.995$	RSD $\leq$ 15% for all analytes or least squares regression $R > 0.995$	RSD $\leq$ 15%, or COD r2 $\geq$ 0.995	%RSD $\leq$ 20%	RSD for each analyte <20%; For analytes with RSD >20%, linear least squares regression with equal weighting factor $R \geq 0.99$, or linear least squares regression with inverse of concentration weighting factor $R \geq 0.99$, or linear least squares regression with inverse square of concentration weighting factor $R \geq 0.99$, or quadratic least squares regression with equal weighting factor $R \geq 0.99$ (requires a minimum of 6 points)	%RSD $\leq$ 20%	RSD < 10% for all analytes or, if the RSD $\geq$ 10% for any analyte, the mean RSD for all analytes in the calibration is <10%
Continuing Calibration Verification	Daily, Weekly, Monthly, Semi-Annual, & Annual	Every 10 samples and at the end of the analytical sequence	Prior to sample analysis, after every 10 field samples and at the end of the analytical sequence.	Every 10 samples and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.	Beginning and before end of daily analytical sequence	Daily prior to sample analysis, every 20 field samples within a 12 hour shift, and at the end of the analytical sequence
Internal Standards (if internal standard calibration is used - each sample IS)	Yes	Yes	Yes	--	--	--	--	--	Yes	Yes	--
Surrogate Standards	--	--	--	--	--	--	--	--	Yes	Yes	Yes
Retention Time Window Establishment	--	--	Yes	Yes	--	Yes	Yes	Yes	Yes	Yes	Yes
Reagent/Method Blanks	1 per batch	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Matrix Spike and Matrix Spike Duplicates	--	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 10 samples
Laboratory Control Sample	1 per 100 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 10 samples
Duplicates	1 per 100 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 10 samples
Interference Check Sample	--	Yes	Yes	--	--	--	--	--	--	--	--
Serial dilution	--	Yes	--	--	--	--	--	--	--	--	--

Notes:
-- - not applicable
CCC - continuing calibration verification
COD - coefficient of determination
hr. - hour
ng/ml - nanograms per milliliter
QC - quality control
RF - response factor
RSD - relative standard deviation
SIM - selective ion monitoring

Table 7
Laboratory QC Requirements
Omega Superfund Site Operable Unit 2

	624	625	625 SIM	1613	1625 (M)	1640	2540 C	4500 CN-E	6010B	7471A	7196A
Initial Calibration (Minimum No. of pts.)	3	5	5	6	5	6	3	1	2	5	6
Initial Calibration Acceptance Criteria	RSD for each analyte <35%; For analytes with RSD >35%, linear least squares regression R ≥ 0.99, or linear least squares regression with inverse of concentration weighting factor R ≥ 0.99, or linear least squares regression with inverse square of concentration weighting factor R ≥ 0.99, or quadratic least squares regression with equal weighting factor R ≥ 0.99 (requires a minimum of 6 points)	RSD for RFs for CCCs ≤30%, the averaged RF for SPCCs is ≥ 0.050, and RSD for each analyte ≤ 15%; if the RSD > 15% for any analyte, the mean RSD for all analytes in the calibration is ≤15%	RSD for RFs for CCCs ≤30% and RSD for each analyte ≤ 15%	10 ng/ml Calibration Verification Standard (VER) retuns value of 8.2 - 12.3 ng/ml	%RSD ≤ 15%	R ≥ 0.995 for each analyte	Analytical Balance Calibration Check ±0.1% of certified weight value	Linear least squares regression R ≥ 0.995, and %D for standards ≥ 0.20ppm is ≤ 10%, and %D for standards < 0.20ppm is ≤ 25%	No acceptance criteria unless more than one standard is used, in which case R ≥ 0.995	R ≥ 0.995	R ≥ 0.995
Continuing Calibration Verification	Daily prior to sample analysis and every 24 hours thereafter at the beginning of an analytical batch.	Daily prior to sample analysis and every 12 hours thereafter during analysis	Daily prior to sample analysis and every 12 hours thereafter during analysis	Every 12 hr.	Every 12 hr.	Daily after every batch of 10 samples or portion thereof, and at the end of the analytical sequence	Daily	Daily	Every 10 samples and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Prior to every batch, every 15 samples, and at the end of the analytical sequence
Internal Standards (if internal standard calibration is used - each sample IS)	Yes	Yes	Yes	Yes	Yes	Yes	--	--	Yes	--	--
Surrogate Standards	Yes	Yes	Yes	Yes	Yes	--	--	--	--	--	--
Retention Time Window Establishment	Yes	Yes	Yes	Yes	Yes	--	--	--	--	--	--
Reagent/Method Blanks	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	--	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Matrix Spike and Matrix Spike Duplicates	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	NA	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	--	--	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Laboratory Control Sample	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	--	--	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Duplicates	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	NA - Client/project discretion	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Interference Check Sample	--	--	--	-	--	--	--	--	Yes	--	--
Serial dilution	--	--	--	-	--	--	--	--	Yes	--	--

Notes:
-- - not applicable
CCC - continuing calibration verification
COD - coefficient of determination
hr. - hour
ng/ml - nanograms per milliliter
QC - quality control
RF - response factor
RSD - relative standard deviation
SIM - selective ion monitoring

Table 7
Laboratory QC Requirements
Omega Superfund Site Operable Unit 2

	8015B (M)	8081A	8082	8151	8260B	8270C	8270C SIM	DHS LUFT
Initial Calibration (Minimum No. of pts.)	5	5	5	5	5	5	5	4
Initial Calibration Acceptance Criteria	RSD ≤ 20% for all analytes or least squares regression R > 0.995	RSD ≤ 20% for all analytes or least squares regression R > 0.995	RSD ≤ 20% for all analytes or least squares regression R > 0.995	RSD ≤ 20% for all analytes, including surrogate	RSD for RFs for CCCs ≤30%; and RSD for each analyte ≤ 15%, or linear least squares regression R ≥ 0.99 when RSD >15%, or non-linear – COD r^2 ≥ 0.99 (minimum of 6 points)	RSD for RFs for CCCs ≤30%; and RSD for each analyte ≤ 15%, or linear least squares regression R ≥ 0.99 when RSD >15%, or non-linear – COD r^2 ≥ 0.99 (minimum of 6 points)	RSD for RFs for CCCs ≤30%; and RSD for each analyte ≤ 15%, or linear least squares regression R ≥ 0.99 when RSD >15%, or non-linear – COD r^2 ≥ 0.99 (minimum of 6 points)	R ≥ 0.995
Continuing Calibration Verification	Every 12 hr. and at the end of the analytical sequence	Every 10 samples and at the end of the analytical sequence	Every 20 samples and at the end of the analytical sequence	Every 20 samples and at the end of the analytical sequence	Every 12 hr.	Every 12 hr.	Every 12 hr.	Every 10 samples and at the end of the analytical sequence
Internal Standards (if internal standard calibration is used - each sample IS)	--	--	--	--	Yes	Yes	Yes	--
Surrogate Standards	Yes	Yes	Yes	Yes	Yes	Yes	Yes	--
Retention Time Window Establishment	Yes	Yes	Yes	Yes	Yes	Yes	Yes	--
Reagent/Method Blanks	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Matrix Spike and Matrix Spike Duplicates	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Laboratory Control Sample	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Duplicates	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples	1 per analytical or preparation batch, not to exceed 20 samples
Interference Check Sample	--	--	--	--	--	--	--	--
Serial dilution	--	--	--	--	--	--	--	--

Notes:
-- - not applicable
CCC - continuing calibration verification
COD - coefficient of determination
hr. - hour
ng/ml - nanograms per milliliter
QC - quality control
RF - response factor
RSD - relative standard deviation
SIM - selective ion monitoring

Table 8
Instrument Preventative Maintenance
Omega Superfund Site Operable Unit 2

Instruments	Maintenance Procedures/Schedule	Spare Parts
Multiparameter Water Quality Meter (dissolved oxygen, conductivity, temperature, pH, ORP, optional barometric pressure)	1. Calibrate at the beginning and end of each day and as necessary during use with solutions specified in manual. 2. Store unit with sensors and probes in transport/calibration cup with tap water to keep them moist. 3. Check battery and recharge/change when low. 4. Replace/clean electrodes, sensors, membranes and membrane caps as needed. 5. Upgrade Software as necessary. 6. Clean instrument as necessary and store in carrying case. 7. Replace expired calibration solutions.	1. Batteries 2. Optional Rechargeable Battery Pack 3. Dissolved Oxygen Electrode Module 4. Dissolved Oxygen Membranes 5. pH and pH/ORP Sensors
Turbidimeter	1. Calibrate at the beginning and end of each day and as necessary during use with solutions specified in manual. 2. Check battery and recharge/change when low. 3. Clean sample tubes before and after each sample. 4. Replace sample tubes that are badly scratched or stained. 5. Maintain sample chamber clean and dry. 6. Replace expired calibration solutions. 7. Store instrument in carrying case. 8. Replace lamp as necessary.	1. Battery 2. AC Adapter 3. 1.0 NTU Turbidity Standard 4. 10.0 NTU Turbidity Standard 5. Turbidity Tubes
Water Level Meter	1. Check battery and change when low. 2. Replace probe as needed. 3. Replace/repair damaged tape as necessary. 4. Check connections. Repair any loose/disconnected wires. 5. Store instrument in carrying bag and with tape rewound onto the reel. 6. Wipe probe clean and dry and place into probe holder after each use.	1. Standard 9-volt Battery 2. Replacement Probe
Photoionization Detector	1. Perform calibration every day. 2. Check battery and recharge/change when low. 3. Keep instrument dry. 4. Keep filter clean.	1. Battery 2. Replacement Lamp 3. Change filter if clogged.

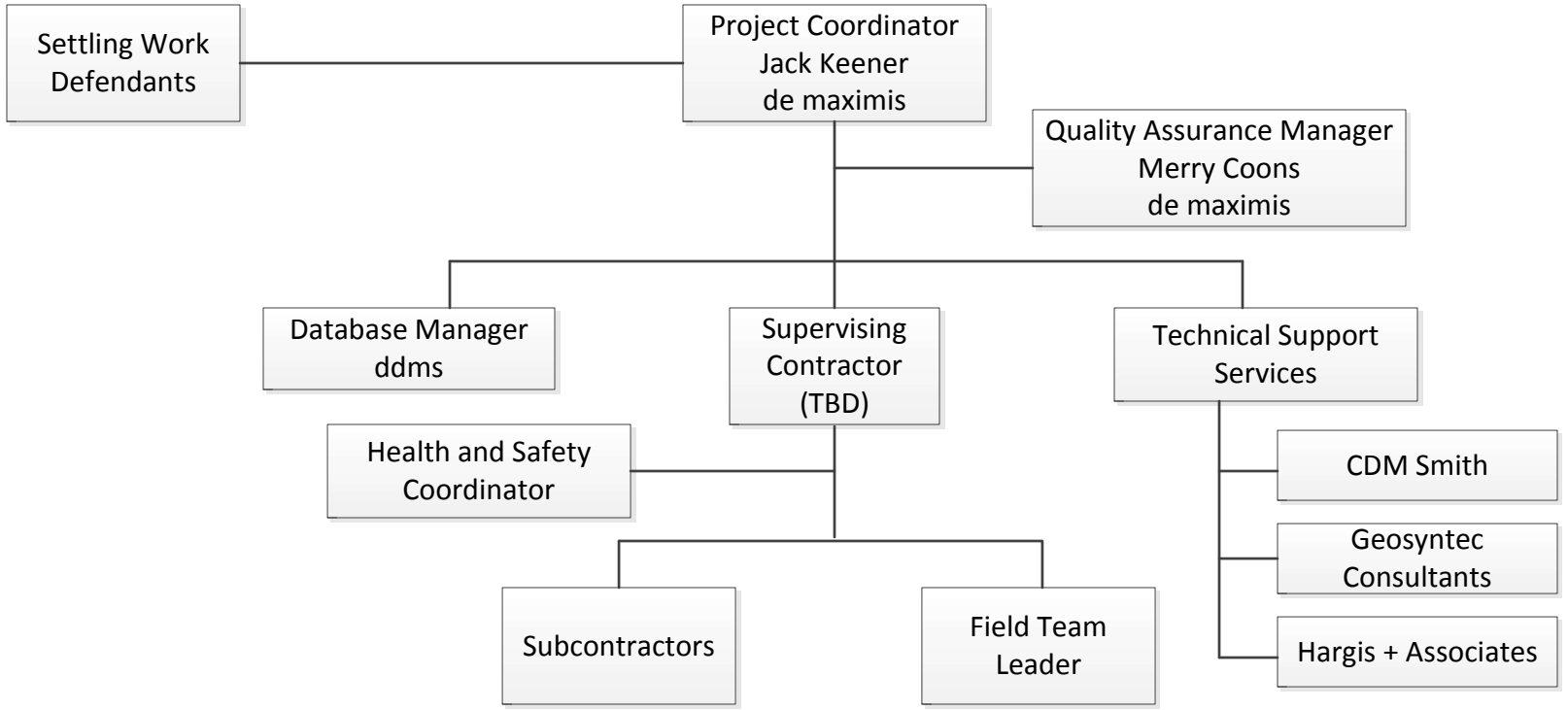
Notes:
AC - alternating current
NTU - Nephelometric Turbidity Unit
ORP - Oxidation-Reduction Potential

Table 9
Hardcopy Data Package Format
Omega Superfund Site Operable Unit 2

Data Component	Description
Case Narrative	Client's sample ID and laboratory ID; Methodology used; Met or exceeded holding times; Description of all analytical and/or receipt problems; QA/QC sample results exceedances; and Authorization of laboratory manager.
COC Documentation	Date and time of sampling and shipping; Sampler and shipper names and signatures; Type of sample; Analyses requested; Project, site, and sampling station names; Date and time of sample receipt; Laboratory sample receiver name and signature; Observed sample condition at time of receipt; Sample/cooler temperature at time of receipt; Air bill numbers; Custody seal; and Sample numbers.
Summary of Sample Results	Laboratory name; Project name, Client's sample ID and lab ID; Sample collection dates; Sample matrix, Dates and times of sample extraction and analysis; Dilution or concentration factor for sample; Method detection limits or quantitation limits; Analytical results and associated units; and Definitions for any laboratory data qualifiers used.
Summary of QA/QC Results	Laboratory name; Project name; Date and time of analysis; Sample matrix; Associated units; Method blank analysis; Surrogate standard recovery; Internal standard analysis; Lab control analysis; Matrix spike and matrix spike duplicate analysis; Duplicate Analysis (when applicable); Instrument calibration (when applicable); Compound confirmation via retention times for each compound (when applicable); and Peak resolution summary (when applicable).
Raw Data (when applicable)	Appropriately scaled chromatograms; Appropriately scaled before and after manual integrations; Area printouts or quantitation reports; Instrument analysis logs for each instrument used; Sample extraction and clean-up logs; Standards preparation logs; Mass spectrometer tuning and mass calibration (when applicable).

Notes:
QA/QC = quality assurance/quality control
COC = chain of custody

FIGURE



Notes:

Project Organization

Omega Superfund Site – OU2
Los Angeles County, California

Geosyntec consultants

Figure

1

WR2209 | October 2016

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APPENDIX A

Analytical Laboratory QA Manual

National
Environmental Laboratory Accreditation Program

OREGON

Environmental Laboratory Accreditation Program

NELAP Recognized

Eurofins Calscience, Inc.

CA300001

7440 Lincoln Way

Garden Grove,CA 92841-1427

IS GRANTED APPROVAL BY ORELAP UNDER THE 2009 TNI STANDARDS, TO PERFORM ANALYSES ON ENVIRONMENTAL SAMPLES IN MATRICES AS LISTED BELOW :

Air	*Drinking Water*	*Non Potable Water*	*Solids and Chem. Waste*	*Tissue*
Chemistry	Chemistry	Chemistry	Chemistry	

AND AS RECORDED IN THE LIST OF APPROVED ANALYTES, METHODS, ANALYTICAL TECHNIQUES, AND FIELDS OF TESTING ISSUED CONCURRENTLY WITH THIS CERTIFICATE AND REVISED AS NECESSARY.

ACCREDITED STATUS DEPENDS ON SUCCESSFUL ONGOING PARTICIPATION IN THE PROGRAM AND CONTINUED COMPLIANCE WITH THE STANDARDS.

CUSTOMERS ARE URGED TO VERIFY THE LABORATORY'S CURRENT ACCREDITATION STATUS IN OREGON.

Gary K. Ward

Gary K. Ward, MS

Oregon State Public Health Laboratory

ORELAP Administrator

3150 NW. 229th Ave, Suite 100

Hillsboro, OR 97124

ISSUE DATE: 01/30/2016

EXPIRATION DATE: 01/29/2017

Certificate No: CA300001 - 010

Oregon

Environmental Laboratory Accreditation Program

Department of Agriculture, Laboratory Division
Department of Environmental Quality, Laboratory Division
Oregon Health Authority, Public Health Division

NELAP Recognized

ORELAP Fields of Accreditation

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As of 01/30/2016 ***this list supercedes all previous lists for this certificate number.***
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MATRIX : Air

Reference	Code	Description
ASTM D1946-90	**30024465**	**Reformed Gas by Gas Chromatography**

Analyte Code	*Analyte*
3755	Carbon dioxide
3780	Carbon monoxide
1767	Helium
1772	Hydrogen
4926	Methane
1843	Nitrogen
3895	Oxygen

EPA RSK-175 (GC-FID)	**10212905**	**Methane, Ethane, and Ethene in water by Headspace GC/FID**

Analyte Code	*Analyte*
3755	Carbon dioxide
4747	Ethane
4752	Ethene
4926	Methane
5029	n-Propane

EPA TO-13A	**10248405**	**Polycyclic Aromatic Hydrocarbons in Ambient Air by GC/MS**

Analyte Code	*Analyte*
5500	Acenaphthene
5505	Acenaphthylene
5555	Anthracene
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5600	Benzo(k)fluoranthene
5855	Chrysene
5895	Dibenz(a,h) anthracene
6265	Fluoranthene
6270	Fluorene
6315	Indeno(1,2,3-cd) pyrene
5005	Naphthalene
6615	Phenanthrene
6665	Pyrene

EPA TO-14A	**10248609**	**Volatile Organic Compounds with SUMMA canister and GC/MS**

Analyte Code	*Analyte*
5160	1,1,1-Trichloroethane

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Analyte Code	*Analyte*
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4375	Benzene
5635	Benzyl chloride
4395	Bromodichloromethane
4400	Bromoform
4455	Carbon tetrachloride
4475	Chlorobenzene
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4645	cis-1,2-Dichloroethylene
4625	Dichlorodifluoromethane (Freon-12)
4765	Ethylbenzene
4835	Hexachlorobutadiene
4950	Methyl bromide (Bromomethane)
4975	Methylene chloride (Dichloromethane)
5100	Styrene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5235	Vinyl chloride
5260	Xylene (total)

EPA TO-15 **10248803** **VOCs collected in Canisters by GC/MS**

Analyte Code	*Analyte*
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4410	2-Butanone (Methyl ethyl ketone, MEK)
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone

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Analyte Code	*Analyte*
4375	Benzene
5635	Benzyl chloride
4395	Bromodichloromethane
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4475	Chlorobenzene
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4625	Dichlorodifluoromethane (Freon-12)
4765	Ethylbenzene
4835	Hexachlorobutadiene
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
5000	Methyl tert-butyl ether (MTBE)
4975	Methylene chloride (Dichloromethane)
4855	n-Hexane
5100	Styrene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

EPA TO-15 GC/MS SIM **10248858** **VOCs collected in Canisters by GC/MS SIM**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
9396	1,2-Epoxybutane
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
9576	1,3-Propane sultone
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4917	1-Butene

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Analyte Code	*Analyte*
4477	1-Chloro-1,2,2-trifluoroethane (Freon 133)
4832	1-Hexene
4833	1-Pentene
4836	1-Propene (Propylene)
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
4666	2,2-Dimethylbutane
4667	2,3,4-Trimethylpentane
4669	2,3-Dimethylbutane
4671	2,3-Dimethylpentane
4672	2,4-Dimethylpentane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4535	2-Chlorotoluene
4538	2-Ethyltoluene
4860	2-Hexanone (MBK)
4863	2-Hexene
4934	2-Methyl-2-Butene
4938	2-Methylbutane (Isopentane)
4939	2-Methylheptane
4946	2-Methylhexane
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
6400	2-Methylphenol (o-Cresol)
4942	2-methylpropane (Isobutane)
5020	2-Nitropropane
4531	3-Ethyltoluene
4529	3-Methyl-1-Butene
4532	3-Methylheptane
4533	3-Methylhexane
4534	3-Methylpentane
4540	4-Chlorotoluene
4542	4-Ethyltoluene
4910	4-Isopropyltoluene (p-Cymene)
4913	4-Methyl-1-Pentene
4995	4-Methyl-2-pentanone (MIBK)
4300	Acetaldehyde
4315	Acetone
4320	Acetonitrile
5510	Acetophenone
4323	Acetylene
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4355	Allyl chloride (3-Chloropropene)
6698	alpha-Pinene
4375	Benzene
5635	Benzyl chloride
5075	beta-Propiolactone
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4398	Bromoethene
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride

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Analyte Code	*Analyte*
7215	Carbonyl sulfide
7235	Catechol
9336	Chloroacetic acid
4475	Chlorobenzene
4575	Chlorodibromomethane
4577	Chlorodifluoromethane (Freon-22)
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4525	Chloroprene (2-Chloro-1,3-butadiene)
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4602	cis-2-Butene
4604	cis-2-Hexene
4603	cis-2-pentene
7325	Cresol/Cresylic acid (mixed isomers)
4555	Cyclohexane
4562	Cyclopentane
4563	Cyclopentene
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
6080	Diethyl sulfate
7480	Dimethyl carbamoyl chloride
7485	Dimethyl sulfate
6208	d-Limonene
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4747	Ethane
4750	Ethanol
4752	Ethene
4755	Ethyl acetate
4760	Ethyl acrylate
6250	Ethyl carbamate (Urethane)
4765	Ethylbenzene
4795	Ethylene oxide
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
6317	Isoheptane
6320	Isophorone
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4930	Methanol
4940	Methyl acetate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
9498	Methyl isocyanate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5245	m-Xylene
5010	n, n-Dimethyl formamide
5005	Naphthalene
5007	n-Butane
4415	n-Butyl-acetate

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Analyte Code	*Analyte*
4435	n-Butylbenzene
5875	n-Decane
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
6530	n-Nitrosodimethylamine
6555	n-Nitrosomorpholine
6520	n-Nitroso-n-methylurea
5026	n-Nonane
5027	n-Octane
5028	n-Pentane
5029	n-Propane
5055	n-Propanol
5090	n-Propylbenzene
6747	n-Undecane
5250	o-Xylene
5253	p-Diethylbenzene
6625	Phenol
7995	Phosgene
6935	Propanal (Propionaldehyde)
9579	Propylene oxide
5255	p-Xylene
4440	sec-Butylbenzene
5100	Styrene
9594	Styrene oxide
4370	T-amylmethylether (TAME)
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4607	trans-2-Butene
4606	trans-2-Hexene
4608	trans-2-pentene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5202	Trifluoromethane (Freon 23)
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5260	Xylene (total)

EPA TO-17 **10312206** **Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes**

Analyte Code	*Analyte*
5160	1,1,1-Trichloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene

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Analyte Code	*Analyte*
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
5220	2,2,4-Trimethylpentane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4375	Benzene
4395	Bromodichloromethane
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4475	Chlorobenzene
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4625	Dichlorodifluoromethane (Freon-12)
4765	Ethylbenzene
4835	Hexachlorobutadiene
4900	Isopropylbenzene
5240	m+p-xylene
4960	Methyl chloride (Chloromethane)
5000	Methyl tert-butyl ether (MTBE)
4975	Methylene chloride (Dichloromethane)
4855	n-Hexane
5250	o-Xylene
5100	Styrene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

EPA TO-3 **10249000** **Cryogenic Trapping**

Analyte Code	*Analyte*
9408	Gasoline range organics (GRO)
4926	Methane

EPA TO-4A **10249204** **Pesticides and PCBs by HV PUF GC**

Analyte Code	*Analyte*
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)

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Analyte Code	*Analyte*
8913	Aroclor-1268 (PCB-1268)
7115	beta-BHC (beta-Hexachlorocyclohexane)
7250	Chlordane (tech.)
7105	delta-BHC
7470	Dieldrin
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7120	gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
7810	Methoxychlor
8250	Toxaphene (Chlorinated camphene)

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MATRIX : Drinking Water

Reference	Code	Description
EPA 150.1	**10008205**	**pH - Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 160.1	**10009004**	**Total Dissolved Solids, dried @ 180 C.**

Analyte Code	*Analyte*
1705	Total dissolved solids

EPA 160.2	**10256403**	**Total Suspended Solids, 0.2um dried @105C**

Analyte Code	*Analyte*
1960	Residue-nonfilterable (TSS)

EPA 160.3	**10009800**	**Total Solids, dried @ 103-105 C.**

Analyte Code	*Analyte*
1950	Residue-total

EPA 160.4	**10010409**	**Total Volatile Solids, ignition @ 550 C.**

Analyte Code	*Analyte*
1970	Residue-volatile
2070	Volatile suspended solids

EPA 160.4	**10256801**	**Total Volatile Solids, ignition @ 550 C.**

Analyte Code	*Analyte*
1970	Residue-volatile
2070	Volatile suspended solids

EPA 160.5	**10010603**	**Settleable solids**

Analyte Code	*Analyte*
1965	Residue-settleable

EPA 180.1	**10011402**	**Turbidity - Nephelometric**

Analyte Code	*Analyte*
2055	Turbidity

EPA 200.7 4.4	**10013806**	**ICP - metals**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1034	Cerium
1040	Chromium
1050	Cobalt

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Analyte Code	*Analyte*
1055	Copper
1060	Gold
1760	Hardness (calc.)
1063	Indium
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium
1183	Tungsten
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 200.8 5.4 **10014605** **Metals by ICP-MS**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1145	Silicon
1150	Silver
1155	Sodium

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Analyte Code	*Analyte*
1160	Strontium
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium
3035	Uranium
1185	Vanadium
1190	Zinc

EPA 218.6 **10027802** **Dissolved Hexavalent Chromium by Ion Chromatography**

Analyte Code	*Analyte*
1045	Chromium VI

EPA 245.1 4.1 **10271008** **Mercury by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*
1095	Mercury

EPA 300.0 2.1 **10053200** **Methods for the Determination of Inorganic Substances in Environmental Samples**

Analyte Code	*Analyte*
1540	Bromide
1575	Chloride
1730	Fluoride
1810	Nitrate as N
1820	Nitrate-nitrite
1840	Nitrite as N
1870	Orthophosphate as P
1910	Phosphorus, total
2000	Sulfate

EPA 314.0 **10055400** **Perchlorate in Drinking Water by Ion Chromatography**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 331.0 1.0 **10059708** **Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Mass Spectrometry (LC/ESI/MS)**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 353.2 **10067206** **Nitrate/Nitrite Nitrogen - Automated, Cadmium**

Analyte Code	*Analyte*
1810	Nitrate as N
1820	Nitrate-nitrite
1840	Nitrite as N
1825	Total nitrate+nitrite

EPA 365.1 **10069600** **Phosphorous - Colorimetric, Automated persulfate**

Analyte Code	*Analyte*
1870	Orthophosphate as P

EPA 504.1 **10082607** **EDB/DBCP/TCP micro-extraction, GC/ECD**

Analyte Code	*Analyte*
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)

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EPA 524.2 4.1 **10088809** **Volatile Organic Compounds GC/MS Capillary Column**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
7450	1,1-Dichloro-2-propanone
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4620	1,4-Dichlorobenzene
4480	1-Chlorobutane
4510	1-Chlorohexane
4665	2,2-Dichloropropane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4860	2-Hexanone (MBK)
5020	2-Nitropropane
4536	4-Bromofluorobenzene
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4325	Acrolein (Propenal)
4340	Acrylonitrile
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4555	Cyclohexane
4595	Dibromomethane (Methylene bromide)

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Analyte Code	*Analyte*
4625	Dichlorodifluoromethane (Freon-12)
9375	Di-isopropylether (DIPE)
4765	Ethylbenzene
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
4900	Isopropylbenzene
5240	m+p-xylene
4940	Methyl acetate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
5000	Methyl tert-butyl ether (MTBE)
4975	Methylene chloride (Dichloromethane)
5245	m-Xylene
5005	Naphthalene
4435	n-Butylbenzene
5015	Nitrobenzene
5090	n-Propylbenzene
5250	o-Xylene
5035	Pentachloroethane
5255	p-Xylene
4440	sec-Butylbenzene
5100	Styrene
4370	T-amylmethylether (TAME)
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

SM 2130 B 21st ED **20042608** **Turbidity by Nephelometric Method**

Analyte Code	*Analyte*
2055	Turbidity

SM 2320 B 21st ED **20045403** **Alkalinity by Titration Method**

Analyte Code	*Analyte*
1505	Alkalinity as CaCO3

SM 2340 B 21st ED **20046406** **Hardness by calculation**

Analyte Code	*Analyte*
1750	Hardness

SM 2340 C 21st ED **20047409** **Hardness by EDTA Titration Method**

Analyte Code	*Analyte*
1750	Hardness

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SM 2510 B 21st ED	**20048402**	**Conductivity by Probe**

Analyte Code	*Analyte*
1610	Conductivity

SM 2540 B 21st ED	**20049201**	**Total Solids Dried at 103 - 105C**

Analyte Code	*Analyte*
1950	Residue-total

SM 2540 C 21st ED	**20050208**	**Total Dissolved Solids Dried at 180C**

Analyte Code	*Analyte*
1955	Residue-filterable (TDS)

SM 2540 D 21st ED	**20051007**	**Total Suspended Solids Dried at 103 - 105C**

Analyte Code	*Analyte*
1960	Residue-nonfilterable (TSS)

SM 2540 E 20th ED	**20051654**	**Total Volatile Solids**

Analyte Code	*Analyte*
1725	Total, fixed, and volatile residue

SM 4500-Cl C 20th ED	**20078802**	**Chlorine by Iodometric Method II**

Analyte Code	*Analyte*
1575	Chloride

SM 4500-CN E 20th ED	**20092404**	**Cyanide by Colorimetric Determination**

Analyte Code	*Analyte*
1635	Cyanide
1645	Total cyanide

SM 4500-CN F 20th ED	**20092802**	**Cyanide by Ion Selective Electrode**

Analyte Code	*Analyte*
1635	Cyanide

SM 4500-CN G 20th ED	**20093203**	**Cyanide Amenable to Chlorination after Distillation**

Analyte Code	*Analyte*
1510	Amenable cyanide

SM 4500-F^- C 21st ED	**20102209**	**Fluoride by Ion-Selective Electrode Method**

Analyte Code	*Analyte*
1730	Fluoride

SM 4500-H+ B 21st ED	**20105004**	**pH Value by Electrometric Method .**

Analyte Code	*Analyte*
1900	pH

SM 4500-NO_2^- B 18th ED	**20024004**	**Nitrite Nitrogen by Colorimetric Determination**

Analyte Code	*Analyte*
1840	Nitrite as N

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SM 4500-NO2¯ B 21st ED **20112805** **Nitrite by Colorimetric Method**

Analyte Code	*Analyte*
1840	Nitrite as N

SM 4500-NO3¯ E 20th ED **20114403** **Nitrate Nitrogen by Cadmium Reduction Method**

Analyte Code	*Analyte*
1805	Nitrate
1810	Nitrate as N
1820	Nitrate-nitrite
1835	Nitrite
1840	Nitrite as N

SM 4500-NO3¯ E 21st ED **20114607** **Nitrate by Cadmium Reduction Method .**

Analyte Code	*Analyte*
1810	Nitrate as N
1820	Nitrate-nitrite

SM 4500-P E 21st ED **20124009** **Phosphorus by Ascorbic Acid Method**

Analyte Code	*Analyte*
1870	Orthophosphate as P
1910	Phosphorus, total
1908	Total Phosphate

SM 5310 B 20th ED **20137400** **Total Organic Carbon by Combustion Infra-red Method**

Analyte Code	*Analyte*
1710	Dissolved organic carbon (DOC)
2040	Total organic carbon

SM 5310 D 20th ED **20139406** **Total Organic Carbon by Wet Oxidation Method**

Analyte Code	*Analyte*
2040	Total organic carbon

SM 5540 C 20th ED **20144609** **Surfactants as MBAS**

Analyte Code	*Analyte*
2025	Surfactants - MBAS

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MATRIX : Non-Potable Water

Reference	Code	Description
EPA 1010	**10116606**	**Pensky-Martens Closed-Cup Method for Determining Ignitability**

Analyte Code	*Analyte*
1780	Ignitability

EPA 120.1	**10006209**	**Conductance - Specific @ 25 C**

Analyte Code	*Analyte*
1610	Conductivity

EPA 1311	**10118806**	**Toxicity Characteristic Leaching Procedure**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 1312	**10119003**	**Synthetic Precipitation Leaching Procedure**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 150.1	**10008205**	**pH - Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 160.1	**10009004**	**Total Dissolved Solids, dried @ 180 C.**

Analyte Code	*Analyte*
1705	Total dissolved solids

EPA 160.2	**10256403**	**Total Suspended Solids, 0.2um dried @105C**

Analyte Code	*Analyte*
1960	Residue-nonfilterable (TSS)

EPA 160.3	**10009800**	**Total Solids, dried @ 103-105 C.**

Analyte Code	*Analyte*
1950	Residue-total

EPA 160.4	**10010409**	**Total Volatile Solids, ignition @ 550 C.**

Analyte Code	*Analyte*
2070	Volatile suspended solids

EPA 160.4	**10256801**	**Total Volatile Solids, ignition @ 550 C.**

Analyte Code	*Analyte*
1970	Residue-volatile

EPA 160.5	**10010603**	**Settleable solids**

Analyte Code	*Analyte*
1965	Residue-settleable

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EPA 1631E **10237204** **Mercury in Water by Oxidation, Purge & Trap, and Cold Vapor Atomic Fluorescence**

Analyte Code	*Analyte*
1095	Mercury

EPA 1640 **10124400** **Trace Elements by Chelation Preconcentration and ICP/MS**

Analyte Code	*Analyte*
1010	Arsenic
1030	Cadmium
1055	Copper
1075	Lead
1105	Nickel
1150	Silver
1190	Zinc

EPA 1664A (HEM) **10127807** **N-Hexane Extractable Material (Oil and Grease) by Extraction and Gravimetry**

Analyte Code	*Analyte*
1803	n-Hexane Extractable Material (O&G)
1860	Oil & Grease
2050	Total Petroleum Hydrocarbons (TPH)

EPA 1664A (SGT-HEM) **10261606** **Silica Gen Treated N-Hexane Extractable Material (Oil and Grease)**

Analyte Code	*Analyte*
1803	n-Hexane Extractable Material (O&G)
1860	Oil & Grease
2050	Total Petroleum Hydrocarbons (TPH)

EPA 180.1 **10011402** **Turbidity - Nephelometric**

Analyte Code	*Analyte*
2055	Turbidity

EPA 200.7 4.4 **10013806** **ICP - metals**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1034	Cerium
1040	Chromium
1045	Chromium VI
1050	Cobalt
1055	Copper
1060	Gold
1760	Hardness (calc.)
1063	Indium
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury

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Analyte Code	*Analyte*
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium
1183	Tungsten
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 200.8 5.4 **10014605** **Metals by ICP-MS**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium
3035	Uranium
1185	Vanadium
1190	Zinc

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EPA 218.6 **10027802** **Dissolved Hexavalent Chromium by Ion Chromatography**

Analyte Code	*Analyte*
1045	Chromium VI

EPA 245.1 4.1 **10271008** **Mercury by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*
1095	Mercury

EPA 300.0 2.1 **10053200** **Methods for the Determination of Inorganic Substances in Environmental Samples**

Analyte Code	*Analyte*
1540	Bromide
1575	Chloride
1730	Fluoride
1810	Nitrate as N
1820	Nitrate-nitrite
1840	Nitrite as N
1870	Orthophosphate as P
1910	Phosphorus, total
2000	Sulfate

EPA 3005A **10133207** **Acid Digestion of waters for Total Recoverable or Dissolved Metals**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3010A **10133605** **Acid Digestion of Aqueous samples and Extracts for Total Metals**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3020A **10134404** **Acid Digestion of Aqueous samples and Extracts for Total Metals for Analysis by GFAA**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3050B **10135601** **Acid Digestion of Sediments, Sludges, and soils**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 314.0 **10055400** **Perchlorate in Drinking Water by Ion Chromatography**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 331.0 1.0 **10059708** **Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Mass Spectrometry (LC/ESI/MS)**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 350.1 **10063204** **Ammonia Nitrogen - Colorimetric, Auto Phenate**

Analyte Code	*Analyte*
1515	Ammonia as N

ORELAP Fields of Accreditation

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Eurofins Calscience, Inc.

7440 Lincoln Way
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EPA 3500B **10137209** **Organic Extraction and sample preparation**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 351.2 **10065006** **Total Kjeldahl Nitrogen - Block Digest, Phenate**

Analyte Code	*Analyte*
1790	Kjeldahl nitrogen

EPA 3510C **10138202** **Separatory Funnel Liquid-liquid extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3511 **10279808** **Organic Compounds in Water by Microextraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3520C **10139001** **Continuous Liquid-liquid extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3545A **10141001** **Pressurized Fluid Extraction (PFE)**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3550B **10141807** **Ultrasonic Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3550C **10142004** **Ultrasonic Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3630C **10146802** **Silica gel cleanup**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 365.1 **10069600** **Phosphorous - Colorimetric, Automated persulfate**

Analyte Code	*Analyte*
1870	Orthophosphate as P
1910	Phosphorus, total

EPA 365.3 **10070801** **Phosphorous - Colorimetric, two reagent.**

Analyte Code	*Analyte*
1870	Orthophosphate as P
1910	Phosphorus, total

EPA 365.4 **10071008** **Phosphorous - Colorimetric, automated block.**

Analyte Code	*Analyte*

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Analyte Code	*Analyte*
1910	Phosphorus, total

EPA 410.1 **10075806** **Chemical Oxygen Demand - Titrimetric (mid-level).**

Analyte Code	*Analyte*
1565	Chemical oxygen demand

EPA 410.4 **10077006** **Chemical Oxygen Demand - Colorimetric, Automated.**

Analyte Code	*Analyte*
1565	Chemical oxygen demand

EPA 413.2 **10078009** **Oil and Grease - Spectrophotometric, Infrared.**

Analyte Code	*Analyte*
1860	Oil & Grease

EPA 418.1 **10079002** **Petroleum Hydrocarbons - Spec. Infrared.**

Analyte Code	*Analyte*
2050	Total Petroleum Hydrocarbons (TPH)

EPA 420.1 **10079206** **Phenolics - Spectrophotometric, manual.**

Analyte Code	*Analyte*
1905	Total phenolics

EPA 5000 **10152600** **Sample Preparation for Volatile Organics**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 5030B **10153409** **Purge and trap for aqueous samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 5030C **10284603** **Purge-and-Trap for Aqueous Samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 524.2 4.1 **10088809** **Volatile Organic Compounds GC/MS Capillary Column**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
7450	1,1-Dichloro-2-propanone
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)

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Analyte Code	*Analyte*
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4620	1,4-Dichlorobenzene
4480	1-Chlorobutane
4510	1-Chlorohexane
4665	2,2-Dichloropropane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4860	2-Hexanone (MBK)
5020	2-Nitropropane
4536	4-Bromofluorobenzene
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4325	Acrolein (Propenal)
4340	Acrylonitrile
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4555	Cyclohexane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4725	Diethyl ether
9375	Di-isopropylether (DIPE)
4810	Ethyl methacrylate
4765	Ethylbenzene
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
4900	Isopropylbenzene
5240	m+p-xylene
4925	Methacrylonitrile
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4990	Methyl methacrylate

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Analyte Code	*Analyte*
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4975	Methylene chloride (Dichloromethane)
5245	m-Xylene
5005	Naphthalene
4435	n-Butylbenzene
5015	Nitrobenzene
5090	n-Propylbenzene
5250	o-Xylene
5035	Pentachloroethane
5080	Propionitrile (Ethyl cyanide)
5255	p-Xylene
4440	sec-Butylbenzene
5100	Styrene
4370	T-amylmethylether (TAME)
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

EPA 6010B **10155609** **ICP - AES**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1057	Gallium
1060	Gold
1760	Hardness (calc.)
1063	Indium
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon

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Analyte Code	*Analyte*
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1175	Tin
1180	Titanium
1183	Tungsten
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 6010C **10155803** **ICP - AES**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1063	Indium
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1175	Tin
1180	Titanium
1183	Tungsten
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 602 **10102202** **Purgeable Aromatics by GC/PID Purge & Trap**

Analyte Code	*Analyte*
4610	1,2-Dichlorobenzene
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4375	Benzene

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Analyte Code	*Analyte*
4765	Ethylbenzene
5240	m+p-xylene
5250	o-Xylene
5140	Toluene
5260	Xylene (total)

EPA 6020 **10156000** **Inductively Coupled Plasma-Mass Spectrometry**

Analyte Code	*Analyte*
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1030	Cadmium
1040	Chromium
1050	Cobalt
1055	Copper
1075	Lead
1100	Molybdenum
1105	Nickel
1140	Selenium
1150	Silver
1165	Thallium
1185	Vanadium
1190	Zinc

EPA 6020A **10156408** **Inductively Coupled Plasma-Mass Spectrometry**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium

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Analyte Code	*Analyte*
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 608 **10103603** **Organochlorine Pesticides & PCBs by GC/ECD**

Analyte Code	*Analyte*
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7005	Alachlor
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)
7065	Atrazine
7115	beta-BHC (beta-Hexachlorocyclohexane)
7160	Butachlor
7250	Chlordane (tech.)
7265	Chloroneb
7310	Chlorthalonil (Daconil)
8550	Dacthal (DCPA)
7105	delta-BHC
7470	Dieldrin
7473	Dimethazone (Clomazone)
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
6285	Hexachlorocyclopentadiene
7725	Isodrin
7740	Kepone
7770	Malathion
7810	Methoxychlor
7825	Methyl parathion (Parathion, methyl)
7835	Metolachlor
7845	Metribuzin
7870	Mirex
7955	Parathion, ethyl
8045	Propachlor (Ramrod)
8125	Simazine
8250	Toxaphene (Chlorinated camphene)
8295	Trifluralin (Treflan)

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EPA 610 (HPLC) **10297004** **Polynuclear Hydrocarbons by HPLC/UV-VIS**

Analyte Code	*Analyte*
6380	1-Methylnaphthalene
6385	2-Methylnaphthalene
5500	Acenaphthene
5505	Acenaphthylene
5555	Anthracene
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5590	Benzo(g,h,i)perylene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5855	Chrysene
5895	Dibenz(a,h) anthracene
6265	Fluoranthene
6270	Fluorene
6315	Indeno(1,2,3-cd) pyrene
5005	Naphthalene
6615	Phenanthrene
6665	Pyrene

EPA 624 **10107207** **Volatile Organic Compounds by purge and trap GC/MS**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)

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Analyte Code	*Analyte*
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4412	2-Chloro-2-methybutane (tert-Amyl chloride)
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4860	2-Hexanone (MBK)
5020	2-Nitropropane
4534	3-Methylpentane
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4320	Acetonitrile
4325	Acrolein (Propenal)
4340	Acrylonitrile
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
4515	bis(Chloromethyl)ether
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4555	Cyclohexane
4560	Cyclohexanone
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4725	Diethyl ether
9375	Di-isopropylether (DIPE)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4930	Methanol
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
5000	Methyl tert-butyl ether (MTBE)

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Analyte Code	*Analyte*
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5245	m-Xylene
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5055	n-Propanol
5090	n-Propylbenzene
5250	o-Xylene
5080	Propionitrile (Ethyl cyanide)
5255	p-Xylene
4440	sec-Butylbenzene
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5260	Xylene (total)

EPA 625 **10300002** **Base/Neutrals and Acids by GC/MS**

Analyte Code	*Analyte*
6703	1,1'-Biphenyl (BZ-0)
6705	1,2,3,4-Tetrachlorobenzene
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6155	1,2-Dinitrobenzene
6221	1,2-Diphenylhydrazine
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
4615	1,3-Dichlorobenzene
6160	1,3-Dinitrobenzene (1,3-DNB)
4620	1,4-Dichlorobenzene
6165	1,4-Dinitrobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6420	1,4-Naphthoquinone
6630	1,4-Phenylenediamine
5790	1-Chloronaphthalene
6380	1-Methylnaphthalene
9501	1-Methylphenanthrene
6425	1-Naphthylamine
4659	2,2'-Oxybis(1-chloropropane)
6735	2,3,4,6-Tetrachlorophenol
6738	2,3,4-Trichlorophenol
6740	2,3,5,6-Tetrachlorophenol

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Analyte Code	*Analyte*
6742	2,3,5-Trichlorophenol
6830	2,3,6-Trichlorophenol (4C)
9363	2,3-Dichloroaniline
5983	2,3-Dichlorophenol
6014	2,3-Dinitrotoluene
6835	2,4,5-Trichlorophenol
6840	2,4,6-Trichlorophenol
5880	2,4-Diaminotoluene
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
5992	2,5-Dichlorophenol
6180	2,5-Dinitrophenol
6183	2,6-Diaminotoluene
6005	2,6-Dichlorophenol
6190	2,6-Dinitrotoluene (2,6-DNT)
5515	2-Acetylaminofluorene
5795	2-Chloronaphthalene
5800	2-Chlorophenol
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6430	2-Naphthylamine
6460	2-Nitroaniline
6490	2-Nitrophenol
6692	2-Terphenyl
6412	3 & 4 Methylphenol
5945	3,3'-Dichlorobenzidine
6120	3,3'-Dimethylbenzidine
6818	3,4,5-Trichlorophenol
5997	3,4-Dichlorophenol
4742	3-Chlorophenol
6355	3-Methylcholanthrene
6405	3-Methylphenol (m-Cresol)
6465	3-Nitroaniline
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
5540	4-Aminobiphenyl
5660	4-Bromophenyl phenyl ether (BDE-3)
5853	4-Chloro-2-methylphenol
5700	4-Chloro-3-methylphenol
5745	4-Chloroaniline
5805	4-Chlorophenol
5825	4-Chlorophenyl phenylether
6105	4-Dimethyl aminoazobenzene
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
6572	6-Chloro-3-methylphenol
6115	7,12-Dimethylbenz(a) anthracene
5500	Acenaphthene
5505	Acenaphthylene
5510	Acetophenone
4330	Acrylamide
7010	Aldicarb (Temik)
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
6700	alpha-Terpineol

ORELAP Fields of Accreditation

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Eurofins Calscience, Inc.

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Analyte Code	*Analyte*
5545	Aniline
5555	Anthracene
7065	Atrazine
5562	Azobenzene
5565	Benzal chloride
5570	Benzaldehyde
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5590	Benzo(g,h,i)perylene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5587	Benzofluoranthene
5610	Benzoic acid
5630	Benzyl alcohol
7115	beta-BHC (beta-Hexachlorocyclohexane)
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
6062	bis(2-Ethylhexyl)adipate
5670	Butyl benzyl phthalate
5680	Carbazole
7205	Carbofuran (Furaden)
7210	Carbofuran phenol
7250	Chlordane (tech.)
7260	Chlorobenzilate
5855	Chrysene
8906	Coelution - 3-Chlorophenol + 4-Chlorophenol
5862	Cresols, Total
7105	delta-BHC
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
7405	Diallate
5895	Dibenz(a,h) anthracene
5905	Dibenzofuran
4625	Dichlorodifluoromethane (Freon-12)
7470	Dieldrin
6070	Diethyl phthalate
7475	Dimethoate
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
8620	Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)
6210	Diphenyl ether (Diphenyl Oxide)
6205	Diphenylamine
8625	Disulfoton
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
6260	Ethyl methanesulfonate
7580	Famphur
6265	Fluoranthene
6270	Fluorene
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7650	Garlon (Triclopyr)
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane

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Analyte Code	*Analyte*
6290	Hexachlorophene
6295	Hexachloropropene
6312	Indene
6315	Indeno(1,2,3-cd) pyrene
7725	Isodrin
6320	Isophorone
6325	Isosafrole
7740	Kepone
6345	Methapyrilene
7810	Methoxychlor
4960	Methyl chloride (Chloromethane)
6375	Methyl methanesulfonate
7825	Methyl parathion (Parathion, methyl)
5005	Naphthalene
5875	n-Decane
6230	n-Docosane
6235	n-Dodecane
6240	n-Eicosane
6300	n-Hexadecane
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6560	n-Nitrosopiperidine
6565	n-Nitrosopyrrolidine
6580	n-Octadecane
6745	n-Tetradecane
8290	o,o,o-Triethyl phosphorothioate
5553	Octachlorostyrene
7955	Parathion, ethyl
6590	Pentachlorobenzene
5035	Pentachloroethane
6600	Pentachloronitrobenzene
6605	Pentachlorophenol
6610	Phenacetin
6615	Phenanthrene
6625	Phenol
7985	Phorate
6640	Phthalic anhydride
6650	Pronamide (Kerb)
6665	Pyrene
5095	Pyridine
6685	Safrole
8200	Tetrachlorvinphos (Stirophos, Gardona) Z-isomer
8235	Thionazin (Zinophos)
8250	Toxaphene (Chlorinated camphene)
5200	Triethylamine

EPA 6850 **10304606** **Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 7196A **10162400** **Chromium Hexavalent colorimetric**

Analyte Code	*Analyte*
1045	Chromium VI

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EPA 7199 **10163005** **Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography**

Analyte Code	*Analyte*
1045	Chromium VI

EPA 7420 **10164406** **Lead by Flame Atomic Absorption**

Analyte Code	*Analyte*
1075	Lead

EPA 7470A **10165807** **Mercury in Liquid Waste by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*
1095	Mercury

EPA 8015B **10173601** **Non-halogenated organics using GC/FID**

Analyte Code	*Analyte*
9369	Diesel range organics (DRO)
4750	Ethanol
9408	Gasoline range organics (GRO)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
9488	Jet Fuel
9409	Kerosene
4930	Methanol
9410	Mineral Spirits
9499	Motor Oil
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
5055	n-Propanol
2050	Total Petroleum Hydrocarbons (TPH)
1935	Total recoverable petroleum hydrocarbons (TRPH)

EPA 8021B **10174808** **Aromatic and Halogenated Volatiles by GC with PID and/or ECD Purge & Trap**

Analyte Code	*Analyte*
4610	1,2-Dichlorobenzene
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4375	Benzene
4765	Ethylbenzene
5000	Methyl tert-butyl ether (MTBE)
5140	Toluene
5260	Xylene (total)

EPA 8081A **10178606** **Organochlorine Pesticides by GC/ECD**

Analyte Code	*Analyte*
8580	2,4'-DDD
8585	2,4'-DDE
8590	2,4'-DDT
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7005	Alachlor
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)

ORELAP Fields of Accreditation

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Analyte Code	*Analyte*
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)
7065	Atrazine
7115	beta-BHC (beta-Hexachlorocyclohexane)
7160	Butachlor
7185	Captafol
7250	Chlordane (tech.)
7260	Chlorobenzilate
7265	Chloroneb
7280	Chloropropylate
7300	Chlorpyrifos
7310	Chlorthalonil (Daconil)
7925	cis-Nonachlor
7965	cis-Permethrin
7340	Cyanazine
8550	Dacthal (DCPA)
7105	delta-BHC
7405	Diallate
4580	Dibromochloropropane
7430	Dichlone
7460	Dicofol
7470	Dieldrin
7473	Dimethazone (Clomazone)
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7575	Etridiazole
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6280	Hexachlorocyclohexanes
6285	Hexachlorocyclopentadiene
7725	Isodrin
7740	Kepone
7770	Malathion
7810	Methoxychlor
7825	Methyl parathion (Parathion, methyl)
7835	Metolachlor
7845	Metribuzin
7870	Mirex
7920	Nitrofen
3890	Oxychlordane
7955	Parathion, ethyl
6600	Pentachloronitrobenzene
7975	Permethrin (total)
7980	Perthane
8045	Propachlor (Ramrod)
6685	Safrole
8125	Simazine
8145	Strobane
8155	Sulfotepp

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Analyte Code	*Analyte*
8210	Tetraethyl pyrophosphate (TEPP)
8250	Toxaphene (Chlorinated camphene)
7970	trans Permethrin
7910	trans-Nanochlor
8295	Trifluralin (Treflan)
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)

EPA 8081B **10178800** **Organochlorine Pesticides by GC/ECD**

Analyte Code	*Analyte*
8580	2,4'-DDD
8585	2,4'-DDE
8590	2,4'-DDT
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7005	Alachlor
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
7115	beta-BHC (beta-Hexachlorocyclohexane)
7185	Captafol
7250	Chlordane (tech.)
7260	Chlorobenzilate
7265	Chloroneb
7280	Chloropropylate
7300	Chlorpyrifos
7310	Chlorthalonil (Daconil)
7925	cis-Nonachlor
7965	cis-Permethrin
7340	Cyanazine
8550	Dacthal (DCPA)
7105	delta-BHC
7405	Diallate
7430	Dichlone
7460	Dicofol
7470	Dieldrin
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7575	Etridiazole
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7655	Halowax-1000
7660	Halowax-1001
7665	Halowax-1013
7670	Halowax-1014
7675	Halowax-1051
7680	Halowax-1099
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6280	Hexachlorocyclohexanes
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
7725	Isodrin
7740	Kepone

ORELAP Fields of Accreditation

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Analyte Code	Analyte
7810	Methoxychlor
7825	Methyl parathion (Parathion, methyl)
7870	Mirex
7920	Nitrofen
8290	o,o,o-Triethyl phosphorothioate
5554	Oxadiazon
3890	Oxychlordane
7955	Parathion, ethyl
7957	PCNB
7975	Permethrin (total)
7980	Perthane
8045	Propachlor (Ramrod)
8060	Propazine
8145	Strobane
8250	Toxaphene (Chlorinated camphene)
7970	trans Permethrin
7910	trans-Nanochlor
8295	Trifluralin (Treflan)
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)

EPA 8082 **10179007** **Polychlorinated Biphenyls (PCBs) by GC/ECD**

Analyte Code	Analyte
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)

EPA 8082A **10179201** **Polychlorinated Biphenyls (PCBs) by GC/ECD**

Analyte Code	Analyte
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)

EPA 8141A **10182000** **Organophosphorous Pesticides by GC/NPD**

Analyte Code	Analyte
4310	Acetochlor
7005	Alachlor
7045	Anilazine
7065	Atrazine
7070	Azinphos-ethyl (Ethyl guthion)
7075	Azinphos-methyl (Guthion)
7125	Bolstar (Sulprofos)
7160	Butachlor
7175	Butylate
7205	Carbofuran (Furaden)
7220	Carbophenothion

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Analyte Code	*Analyte*
7300	Chlorpyrifos
7305	Chlorpyrifos-methyl
7315	Coumaphos
7340	Cyanazine
7377	Deethyl atrazine (Desethyl atrazine)
7382	Deisopropyl atrazine
7390	Demeton
7395	Demeton-o
7385	Demeton-s
7410	Diazinon
8605	Dichloroprop (Dichlorprop)
8610	Dichlorovos (DDVP, Dichlorvos)
7475	Dimethoate
8625	Disulfoton
7550	EPN
7555	EPTC (Eptam, s-ethyl-dipropyl thio carbamate)
7565	Ethion
7570	Ethoprop
7580	Famphur
7600	Fensulfothion
7605	Fenthion
7640	Fonophos (Fonofos)
7765	Linuron (Lorox)
7770	Malathion
7785	Merphos
7825	Methyl parathion (Parathion, methyl)
7835	Metolachlor
7845	Metribuzin
7850	Mevinphos
7880	Monocrotophos
7905	Naled
8290	o,o,o-Triethyl phosphorothioate
7955	Parathion, ethyl
7960	Pendimethalin\ (Penoxalin)
7985	Phorate
8000	Phosmet (Imidan)
8035	Prometon
8045	Propachlor (Ramrod)
8060	Propazine
8110	Ronnel
8125	Simazine
8155	Sulfotepp
8185	Terbufos
8200	Tetrachlorvinphos (Stirophos, Gardona) Z-isomer
8210	Tetraethyl pyrophosphate (TEPP)
8235	Thionazin (Zinophos)
8245	Tokuthion (Prothiophos)
8275	Trichloronate
8295	Trifluralin (Treflan)
8320	Vernolate

EPA 8151A **10183207** **Chlorinated Herbicides by GC/ECD**

Analyte Code	*Analyte*
8655	2,4,5-T
8545	2,4-D
8560	2,4-DB
8600	3,5-Dichlorobenzoic acid
6500	4-Nitrophenol
8505	Acifluorfen
8530	Bentazon

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Analyte Code	*Analyte*
7135	Brominal (Bromoxynil)
8540	Chloramben
8550	Dacthal (DCPA)
8555	Dalapon
8595	Dicamba
8605	Dichloroprop (Dichlorprop)
8620	Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)
7650	Garlon (Triclopyr)
7775	MCPA
7780	MCPP
6605	Pentachlorophenol
8645	Picloram
8650	Silvex (2,4,5-TP)

EPA 8260B **10184802** **Volatile Organic Compounds by purge and trap GC/MS**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4665	2,2-Dichloropropane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4860	2-Hexanone
5145	2-Methylaniline (o-Toluidine)
5020	2-Nitropropane
5050	2-Picoline (2-Methylpyridine)
4530	3-Chloropropionitrile
4540	4-Chlorotoluene
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4320	Acetonitrile
4325	Acrolein (Propenal)
4340	Acrylonitrile
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5635	Benzyl chloride
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane

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Analyte Code	*Analyte*
4395	Bromodichloromethane
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4525	Chloroprene (2-Chloro-1,3-butadiene)
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4627	Dichlorofluoromethane (Freon 21)
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4755	Ethyl acetate
4810	Ethyl methacrylate
4765	Ethylbenzene
4795	Ethylene oxide
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4900	Isopropylbenzene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4975	Methylene chloride (Dichloromethane)
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4435	n-Butylbenzene
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5085	n-Propylamine
5090	n-Propylbenzene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
5095	Pyridine
4440	sec-Butylbenzene
5100	Styrene
4370	T-amylmethylether (TAME)
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)

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Analyte Code	*Analyte*
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

EPA 8260B SIM **10184904** **Volatile Organic Compounds by purge and trap GC/MS-SIM**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
5167	1,1,2-Trichlorofluoroethane
5172	1,1,2-Trifluoroethane
5171	1,1-Dichloro-1-fluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
4656	1,2-diethylbenzene
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4676	1,3-Diethylbenzene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4919	1-Chloro-1,1-difluoroethane
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4411	2-Chloro-1,1,1-trifluoroethane
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene

ORELAP Fields of Accreditation

ORELAP ID: CA300001
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Eurofins Calscience, Inc.

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Analyte Code	*Analyte*
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
6103	3,3'-dimethyl-1-butanol
4530	3-Chloropropionitrile
4534	3-Methylpentane
4536	4-Bromofluorobenzene
5712	4-Chloro-2-nitrophenol
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
9466	4-Nonylphenol diethoxylate
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor
4315	Acetone
4320	Acetonitrile
4323	Acetylene
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4577	Chlorodifluoromethane (Freon-22)
4485	Chloroethane (Ethyl chloride)
4486	Chlorofluoromethane
4505	Chloroform
4522	Chloropentafluoroethane
4525	Chloroprene (2-Chloro-1,3-butadiene)
4526	Chlorotrifluoroethene
4705	cis & trans-1,2-Dichloroethene

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Analyte Code	*Analyte*
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide

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Analyte Code	*Analyte*
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene
5095	Pyridine
6685	Safrole
9607	sec-Butyl Alcohol (2-Butanol)
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
9557	tert-butyl-formate
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
9574	Tetrahydrothiophene
5140	Toluene
4027	Total BTEX
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5237	Vinyl Fluoride
5260	Xylene (total)

EPA 8260C **10307003** **Volatile Organics: GC/MS (capillary column)**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane

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Analyte Code	*Analyte*
5167	1,1,2-Trichlorofluoroethane
5172	1,1,2-Trifluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4919	1-Chloro-1,1-difluoroethane
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4411	2-Chloro-1,1,1-trifluoroethane
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4538	2-Ethyltoluene
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
4530	3-Chloropropionitrile
4531	3-Ethyltoluene (1-Methyl-3-ethylbenzene)
4534	3-Methylpentane
4536	4-Bromofluorobenzene
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)

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Analyte Code	*Analyte*
9466	4-Nonylphenol diethoxylate
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor
4315	Acetone
4320	Acetonitrile
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4486	Chlorofluoromethane
4505	Chloroform
4522	Chloropentafluoroethane
4525	Chloroprene (2-Chloro-1,3-butadiene)
4526	Chlorotrifluoroethene
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide

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Analyte Code	*Analyte*
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5028	n-Pentane
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene

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Analyte Code	*Analyte*
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene
5095	Pyridine
6685	Safrole
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
9574	Tetrahydrothiophene
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5237	Vinyl Fluoride
5260	Xylene (total)

EPA 8260C SIM **10307105** **Volatile Organic Compounds by GC/MS-SIM**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
5167	1,1,2-Trichlorofluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane

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Analyte Code	*Analyte*
4675	1,3-Dichloropropene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
6103	3,3'-dimethyl-1-butanol
4530	3-Chloropropionitrile
4534	3-Methylpentane
4536	4-Bromofluorobenzene
5712	4-Chloro-2-nitrophenol
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor
4315	Acetone
4320	Acetonitrile
4323	Acetylene
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform

ORELAP Fields of Accreditation

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Eurofins Calscience, Inc.

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Analyte Code	*Analyte*
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4525	Chloroprene (2-Chloro-1,3-butadiene)
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol

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Analyte Code	*Analyte*
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene
5095	Pyridine
6685	Safrole
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
9557	tert-butyl-formate
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5260	Xylene (total)

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EPA 8270C **10185805** **Semivolatile Organic compounds by GC/MS**

Analyte Code	*Analyte*
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6155	1,2-Dinitrobenzene
6221	1,2-Diphenylhydrazine
6800	1,3,5-Trichlorobenzene
4615	1,3-Dichlorobenzene
6160	1,3-Dinitrobenzene (1,3-DNB)
4620	1,4-Dichlorobenzene
6165	1,4-Dinitrobenzene
6420	1,4-Naphthoquinone
6630	1,4-Phenylenediamine
5520	1-Acetyl-2-thiourea
5790	1-Chloronaphthalene
6425	1-Naphthylamine
6735	2,3,4,6-Tetrachlorophenol
6835	2,4,5-Trichlorophenol
6840	2,4,6-Trichlorophenol
5880	2,4-Diaminotoluene
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
9636	2,4-Toluene diisocyanate
6005	2,6-Dichlorophenol
6190	2,6-Dinitrotoluene (2,6-DNT)
5515	2-Acetylaminofluorene
5795	2-Chloronaphthalene
5800	2-Chlorophenol
5865	2-Cyclohexyl-4,6-dinitrophenol
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6430	2-Naphthylamine
6460	2-Nitroaniline
6490	2-Nitrophenol
5050	2-Picoline (2-Methylpyridine)
6100	3,3'-Dimethoxybenzidine
6120	3,3'-Dimethylbenzidine
5740	3-Chloroaniline
6355	3-Methylcholanthrene
6405	3-Methylphenol (m-Cresol)
6465	3-Nitroaniline
5540	4-Aminobiphenyl
5660	4-Bromophenyl phenyl ether
5700	4-Chloro-3-methylphenol
5745	4-Chloroaniline
5825	4-Chlorophenyl phenylether
6105	4-Dimethyl aminoazobenzene
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
6570	5-Nitro-o-toluidine
6115	7,12-Dimethylbenz(a) anthracene
6125	a-a-Dimethylphenethylamine
5500	Acenaphthene
5505	Acenaphthylene

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Eurofins Calscience, Inc.

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Analyte Code	*Analyte*
5510	Acetophenone
5545	Aniline
5555	Anthracene
5560	Aramite
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5590	Benzo(g,h,i)perylene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5610	Benzoic acid
5630	Benzyl alcohol
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
5670	Butyl benzyl phthalate
5680	Carbazole
5855	Chrysene
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5900	Dibenz(a, j) acridine
5895	Dibenz(a,h) anthracene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
6070	Diethyl phthalate
6080	Diethyl sulfate
6075	Diethylstilbestrol
6090	Dihydrosafrole
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
6205	Diphenylamine
6250	Ethyl carbamate (Urethane)
6260	Ethyl methanesulfonate
6265	Fluoranthene
6270	Fluorene
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
6290	Hexachlorophene
6295	Hexachloropropene
6315	Indeno(1,2,3-cd) pyrene
6320	Isophorone
6325	Isosafrole
6335	Maleic anhydride
6375	Methyl methanesulfonate
5005	Naphthalene
6450	Nicotine
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6555	n-Nitrosomorpholine
6560	n-Nitrosopiperidine
6565	n-Nitrosopyrrolidine
5620	p-Benzoquinone (Quinone)
6590	Pentachlorobenzene
6600	Pentachloronitrobenzene

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Analyte Code	*Analyte*
6605	Pentachlorophenol
6610	Phenacetin
6615	Phenanthrene
6625	Phenol
6640	Phthalic anhydride
6650	Pronamide (Kerb)
6660	Propylthiouracil
6665	Pyrene
5095	Pyridine
6680	Resorcinol
6685	Safrole
6695	Strychnine
6750	Thiophenol (Benzenethiol)

EPA 8270C SIM **10242407** **Semivolatile Organic compounds by GC/MS Selective Ion Monitoring**

Analyte Code	*Analyte*
6703	1,1'-Biphenyl (BZ-0)
6715	1,2,4,5-Tetrachlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6380	1-Methylnaphthalene
5795	2-Chloronaphthalene
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6412	3 & 4 Methylphenol
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
5500	Acenaphthene
5505	Acenaphthylene
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
5555	Anthracene
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
7115	beta-BHC (beta-Hexachlorocyclohexane)
5670	Butyl benzyl phthalate
5680	Carbazole
7250	Chlordane (tech.)
5855	Chrysene
7105	delta-BHC
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5895	Dibenz(a,h) anthracene
5905	Dibenzofuran
5910	Dibenzothiophene
7470	Dieldrin
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate

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Analyte Code	*Analyte*
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
6265	Fluoranthene
6270	Fluorene
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
4840	Hexachloroethane
6312	Indene
6315	Indeno(1,2,3-cd) pyrene
7810	Methoxychlor
5005	Naphthalene
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6555	n-Nitrosomorpholine
6590	Pentachlorobenzene
6605	Pentachlorophenol
6608	Perylene
6615	Phenanthrene
6665	Pyrene
5095	Pyridine
6670	Quinoline

EPA 8270D **10186002** **Semivolatile Organic compounds by GC/MS**

Analyte Code	*Analyte*
6705	1,2,3,4-Tetrachlorobenzene
6707	1,2,3,4-Tetrahydronaphthalene
6710	1,2,3,5-Tetrachlorobenzene
5150	1,2,3-Trichlorobenzene
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6155	1,2-Dinitrobenzene
6221	1,2-Diphenylhydrazine
9564	1,2-Phenylenediamine (o-Phenylenediamine)
6800	1,3,5-Trichlorobenzene
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
4615	1,3-Dichlorobenzene
6160	1,3-Dinitrobenzene (1,3-DNB)
4620	1,4-Dichlorobenzene
6165	1,4-Dinitrobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6420	1,4-Naphthoquinone
6630	1,4-Phenylenediamine
9330	1-Chloro-4-nitrobenzene
5790	1-Chloronaphthalene
5792	1-Chloropropane
6380	1-Methylnaphthalene
9501	1-Methylphenanthrene
6425	1-Naphthylamine
187	1-Phenoxy-2-propanol

ORELAP Fields of Accreditation

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Analyte Code	*Analyte*
5754	1-Phenoxy-2-propanol
4659	2,2-Oxybis(1-chloropropane)
6730	2,3,4,5-Tetrachlorophenol
6735	2,3,4,6-Tetrachlorophenol
6740	2,3,5,6-Tetrachlorophenol
5983	2,3-Dichlorophenol
6014	2,3-Dinitrotoluene
6017	2,4 & 2,6-Toluene Diamine
6790	2,4,5-Trichloroaniline
6835	2,4,5-Trichlorophenol
6795	2,4,6-Trichloroaniline
6840	2,4,6-Trichlorophenol
6890	2,4,6-Trinitrobenzene
5930	2,4-Dichloro-6-methylphenol
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
5992	2,5-Dichlorophenol
6180	2,5-Dinitrophenol
6005	2,6-Dichlorophenol
6190	2,6-Dinitrotoluene (2,6-DNT)
5515	2-Acetylaminofluorene
5735	2-Chloroaniline
5795	2-Chloronaphthalene
5800	2-Chlorophenol
5865	2-Cyclohexyl-4,6-dinitrophenol
5866	2-Ethoxyethanol (cellosolve)
5867	2-Fluorobiphenyl
5868	2-Methoxyphenol (Guaiacol)
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6430	2-Naphthylamine
6460	2-Nitroaniline
6490	2-Nitrophenol
9507	2-Nitrotoluene
5050	2-Picoline (2-Methylpyridine)
6692	2-Terphenyl
6412	3 & 4 Methylphenol
5945	3,3'-Dichlorobenzidine
6100	3,3'-Dimethoxybenzidine
6120	3,3'-Dimethylbenzidine
6815	3,4,5-Trichloroguaiacol
5940	3,4-Dichloroaniline
5995	3,4-Dichloronitrobenzene
5997	3,4-Dichlorophenol
9364	3,4-Methylenedioxyamphetamine (MDA)
5527	3-beta-Coprostanol
5740	3-Chloroaniline
4742	3-Chlorophenol
4530	3-Chloropropionitrile
6355	3-Methylcholanthrene
6405	3-Methylphenol (m-Cresol)
6465	3-Nitroaniline
9510	3-Nitrotoluene
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
6365	4,4-Methylenebis(2-chloroaniline)

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Analyte Code	*Analyte*
6825	4,5,6-Trichloroguaiacol
6827	4,5-Dichloro-2-methoxyphenol (4,5-Dichloroguaiacol)
5540	4-Aminobiphenyl
5660	4-Bromophenyl phenyl ether (BDE-3)
5853	4-Chloro-2-methylphenol
5700	4-Chloro-3-methylphenol
5745	4-Chloroaniline
5805	4-Chlorophenol
5825	4-Chlorophenyl phenylether
6105	4-Dimethyl aminoazobenzene
4910	4-Isopropyltoluene (p-Cymene)
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
6510	4-Nitroquinoline 1-oxide
9513	4-Nitrotoluene
6513	4-Nonylphenol
6516	4-tert-Butylphenol
6570	5-Nitro-o-toluidine
6572	6-Chloro-3-methylphenol
6112	6-Methylchrysene
6115	7,12-Dimethylbenz(a) anthracene
9417	7h-Dibenzo(c, g) carbazole
6125	a-a-Dimethylphenethylamine
5500	Acenaphthene
5505	Acenaphthylene
4310	Acetochlor
5510	Acetophenone
4330	Acrylamide
5445	Aflatoxin B1
5450	Aflatoxin B2
5455	Aflatoxin G1
5460	Aflatoxin G2
7005	Alachlor
7010	Aldicarb (Temik)
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
4357	alpha-Methylstyrene
6700	alpha-Terpineol
9367	Amphetamine
5545	Aniline
5555	Anthracene
5560	Aramite
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)
7055	Asulam
7065	Atrazine
7070	Azinphos-ethyl (Ethyl guthion)
7075	Azinphos-methyl (Guthion)
5562	Azobenzene
5565	Benzal chloride
5570	Benzaldehyde
5567	Benzenethiol (Phenylmercaptan)

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Analyte Code	*Analyte*
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5610	Benzoic acid
5625	Benzotrichloride
5630	Benzyl alcohol
5635	Benzyl chloride
7115	beta-BHC (beta-Hexachlorocyclohexane)
6437	beta-Pinene
6438	beta-Sitosterol
5640	Biphenyl
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
6062	bis(2-Ethylhexyl)adipate
4515	bis(Chloromethyl)ether
7125	Bolstar (Sulprofos)
7160	Butachlor
5670	Butyl benzyl phthalate
5671	Butyl diphenyl Phosphate
7175	Butylate
5673	Butylated Hydroxy Toluene (BHT)
5675	Caffeine
7180	Caprolactam
5680	Carbazole
7205	Carbofuran (Furaden)
7210	Carbofuran phenol
7220	Carbophenothion
7255	Chlorfenvinphos
7260	Chlorobenzilate
7300	Chlorpyrifos
5683	Cholesterol
5855	Chrysene
8906	Coelution - 3-Chlorophenol + 4-Chlorophenol
6414	Coelution - 3-Phenoxyphenol + 4-Phenoxyphenol
7315	Coumaphos
5862	Cresols, Total
7330	Crotoxyphos
7340	Cyanazine
7377	Deethyl atrazine (Desethyl atrazine)
7382	Deisopropyl atrazine
7105	delta-BHC
7390	Demeton
7395	Demeton-o
7385	Demeton-s
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
7405	Diallate
7410	Diazinon
9354	Dibenz(a, h) acridine
5900	Dibenz(a, j) acridine
5895	Dibenz(a,h) anthracene
9348	Dibenzo(a, h) pyrene
9351	Dibenzo(a, i) pyrene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
5910	Dibenzothiophene

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Analyte Code	*Analyte*
5912	Dibutyl phenyl Phospahate
4625	Dichlorodifluoromethane (Freon-12)
8610	Dichlorovos (DDVP, Dichlorvos)
7460	Dicofol
7465	Dicrotophos
7470	Dieldrin
9369	Diesel range organics (DRO)
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
7473	Dimethazone (Clomazone)
7474	Dimetheneamid
7475	Dimethoate
6135	Dimethyl phthalate
6137	Dimethyl terphthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
8620	Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)
7495	Dioxathion
6210	Diphenyl ether (Diphenyl Oxide)
6205	Diphenylamine
8625	Disulfoton
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7550	EPN
7555	EPTC (Eptam, s-ethyl-dipropyl thio carbamate)
7560	Ethalfluralin (Sonalan)
7565	Ethion
7570	Ethoprop
6260	Ethyl methanesulfonate
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
7580	Famphur
7600	Fensulfothion
7605	Fenthion
7625	Fluchloralin
6265	Fluoranthene
6270	Fluorene
7640	Fonophos (Fonofos)
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
6290	Hexachlorophene
6295	Hexachloropropene
6312	Indene
6315	Indeno(1,2,3-cd) pyrene
7725	Isodrin
7727	Isofenphos
6320	Isophorone
6321	Isoquinoline
6325	Isosafrole
7740	Kepone
7770	Malathion
7785	Merphos

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Analyte Code	*Analyte*
7316	Methadone
6342	Methamphetamine
6345	Methapyrilene
7810	Methoxychlor
6375	Methyl methanesulfonate
7825	Methyl parathion (Parathion, methyl)
6377	Methyl styrene
9598	Methyldiethanolamine (MDEA)
9599	Methylenedioxymethamphetamine (MDMA)
7835	Metolachlor
7845	Metribuzin
7850	Mevinphos
7880	Monocrotophos
5010	n, n-Dimethyl formamide
6443	n, n-Dimethylacetamide
7905	Naled
5005	Naphthalene
5875	n-Decane
6300	n-Hexadecane
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6555	n-Nitrosomorpholine
6560	n-Nitrosopiperidine
6565	n-Nitrosopyrrolidine
6580	n-Octadecane
6745	n-Tetradecane
8290	o,o,o-Triethyl phosphorothioate
5553	Octachlorostyrene
3960	o-Phenylphenol
7955	Parathion, ethyl
9537	Pebulate
7960	Pendimethalin\ (Penoxalin)
5872	Pentabromodiphenyl Ether
6590	Pentachlorobenzene
5035	Pentachloroethane
6600	Pentachloronitrobenzene
6605	Pentachlorophenol
6608	Perylene
6610	Phenacetin
6615	Phenanthrene
6625	Phenol
7985	Phorate
8000	Phosmet (Imidan)
6635	Phthalic acid
6640	Phthalic anhydride
9663	p-Phenylenediamine
8035	Prometon
6650	Pronamide (Kerb)
8045	Propachlor (Ramrod)
8060	Propazine
6760	p-Tolualdehyde (1,4-Tolualdehyde)
6665	Pyrene
5095	Pyridine
6670	Quinoline
6683	Retene
8110	Ronnel

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Analyte Code	*Analyte*
6685	Safrole
8125	Simazine
8155	Sulfotepp
8185	Terbufos
6725	Tetrachloroguaiacol
8200	Tetrachlorvinphos (Stirophos, Gardona) Z-isomer
8210	Tetraethyl pyrophosphate (TEPP)
1210	Tetraethyl Tin
8235	Thionazin (Zinophos)
8245	Tokuthion (Prothiophos)
8260	Triallate
8262	Tributyl phosphate
8275	Trichloronate
5200	Triethylamine
8295	Trifluralin (Treflan)
8282	Triphenyl phosphate
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)
8320	Vernolate

EPA 8270D SIM **10242509** **Semivolatile Organic compounds by GC/MS Selective Ion Monitoring**

Analyte Code	*Analyte*
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6221	1,2-Diphenylhydrazine
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6380	1-Methylnaphthalene
9501	1-Methylphenanthrene
6852	2,3,5-Trimethylnaphthalene
6835	2,4,5-Trichlorophenol
6840	2,4,6-Trichlorophenol
5930	2,4-Dichloro-6-methylphenol
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
6188	2,6-Dimethylnaphthalene
6190	2,6-Dinitrotoluene (2,6-DNT)
5795	2-Chloronaphthalene
5800	2-Chlorophenol
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6460	2-Nitroaniline
6490	2-Nitrophenol
6412	3 & 4 Methylphenol
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
5660	4-Bromophenyl phenyl ether (BDE-3)
5700	4-Chloro-3-methylphenol
5825	4-Chlorophenyl phenylether
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
5500	Acenaphthene
5505	Acenaphthylene

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Analyte Code	*Analyte*
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
5555	Anthracene
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5630	Benzyl alcohol
7115	beta-BHC (beta-Hexachlorocyclohexane)
5640	Biphenyl
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
5670	Butyl benzyl phthalate
1201	Butyltin trichloride
5680	Carbazole
5855	Chrysene
7105	delta-BHC
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5895	Dibenz(a,h) anthracene
5905	Dibenzofuran
5910	Dibenzothiophene
5913	Dibutyltin
1202	Dibutyltin dichloride
7470	Dieldrin
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
6265	Fluoranthene
6270	Fluorene
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
4840	Hexachloroethane
6315	Indeno(1,2,3-cd) pyrene
6320	Isophorone
7810	Methoxychlor
1206	Monobutyltin
5005	Naphthalene
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine

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Analyte Code	*Analyte*
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6590	Pentachlorobenzene
6605	Pentachlorophenol
6608	Perylene
6615	Phenanthrene
6625	Phenol
6665	Pyrene
5095	Pyridine
1209	Tetrabutyltin
1213	Tributyltin
1203	Tributyltin chloride

EPA 8310 **10187607** **Polynuclear Aromatic Hydrocarbons by HPLC/UV-VIS**

Analyte Code	*Analyte*
6380	1-Methylnaphthalene
6385	2-Methylnaphthalene
5500	Acenaphthene
5505	Acenaphthylene
5555	Anthracene
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5855	Chrysene
5895	Dibenz(a,h) anthracene
9348	Dibenzo(a, h) pyrene
9351	Dibenzo(a, i) pyrene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
6265	Fluoranthene
6270	Fluorene
6315	Indeno(1,2,3-cd) pyrene
5005	Naphthalene
6615	Phenanthrene
6665	Pyrene

EPA 8330 **10189807** **Nitroaromatics and Nitramines by HPLC/UV-VIS**

Analyte Code	*Analyte*
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
6160	1,3-Dinitrobenzene (1,3-DNB)
9651	2,4,6-Trinitrotoluene (2,4,6-TNT)
6185	2,4-Dinitrotoluene (2,4-DNT)
6190	2,6-Dinitrotoluene (2,6-DNT)
9303	2-Amino-4,6-dinitrotoluene (2-am-dnt)
6462	2-Nitroguanidine
9507	2-Nitrotoluene
9510	3-Nitrotoluene
9306	4-Amino-2,6-dinitrotoluene (4-am-dnt)
9513	4-Nitrotoluene
6415	Methyl-2,4,6-trinitrophenylnitramine (tetryl)
5015	Nitrobenzene
6485	Nitroglycerin
9522	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
9558	Pentaerythritoltetranitrate (PETN)
9432	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)

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EPA 8330A **10190008** **Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)**

Analyte Code	*Analyte*
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
6160	1,3-Dinitrobenzene (1,3-DNB)
9651	2,4,6-Trinitrotoluene (2,4,6-TNT)
5882	2,4-diamino-6-nitrotoluene
6185	2,4-Dinitrotoluene (2,4-DNT)
6181	2,6-diamino-4-nitrotoluene
6190	2,6-Dinitrotoluene (2,6-DNT)
9303	2-Amino-4,6-dinitrotoluene (2-am-dnt)
9507	2-Nitrotoluene
9510	3-Nitrotoluene
9306	4-Amino-2,6-dinitrotoluene (4-am-dnt)
9513	4-Nitrotoluene
7046	Ammonium Picrate
6415	Methyl-2,4,6-trinitrophenylnitramine (tetryl)
9418	MNX
5015	Nitrobenzene
6485	Nitroglycerin
9522	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
9558	Pentaerythritoltetranitrate (PETN)
1899	Picric Acid (2,4,6-Trinitrophenol)
9432	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)

EPA 9014 **10193803** **Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide**

Analyte Code	*Analyte*
1510	Amenable cyanide
1635	Cyanide
1645	Total cyanide

EPA 9040B **10197203** **pH Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 9040C **10244403** **pH Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 9045C **10198400** **Soil and Waste pH**

Analyte Code	*Analyte*
1900	pH

EPA 9056 **10199005** **Determination of Inorganic Anions by Ion Chromatography**

Analyte Code	*Analyte*
1540	Bromide
1575	Chloride
1730	Fluoride
1805	Nitrate
1835	Nitrite
1870	Orthophosphate as P
2000	Sulfate
1825	Total nitrate+nitrite

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EPA SW-846 Chapter 7.3	**10245702**	**Characteristic Determination - Reactivity**

Analyte Code	*Analyte*
1923	Reactive Cyanide
1925	Reactive sulfide

NWTPH-Dx	**90018409**	**Oregon DEQ TPH Diesel Range**

Analyte Code	*Analyte*
9369	Diesel range organics (DRO)
9488	Jet Fuel
9499	Motor Oil
9506	Residual Range Organics (RRO)

NWTPH-Gx	**90018603**	**Oregon DEQ TPH Gasoline Range Organics by GC/FID-PID Purge & Trap**

Analyte Code	*Analyte*
9408	Gasoline range organics (GRO)

Polisini & Miller (CDFG 1988)	**970**	**Static Acute Bioassay Procedures for Hazardous Waste Samples**

Analyte Code	*Analyte*
800	Fathead Minnow (P. promelas)

SM 2120 B 21st ED	**20039003**	**Color by Visual Comparison**

Analyte Code	*Analyte*
1605	Color

SM 2130 B 18th ED	**20042006**	**Turbidity by Nephelometric Determination**

Analyte Code	*Analyte*
2055	Turbidity

SM 2310 B 20th ED	**20044206**	**Acidity by Titration**

Analyte Code	*Analyte*
1500	Acidity, as CaCO3

SM 2320 B 21st ED	**20045403**	**Alkalinity by Titration Method**

Analyte Code	*Analyte*
1505	Alkalinity as CaCO3

SM 2340 B 21st ED	**20046406**	**Hardness by calculation**

Analyte Code	*Analyte*
1750	Hardness

SM 2340 C 21st ED	**20047409**	**Hardness by EDTA Titration Method**

Analyte Code	*Analyte*
1750	Hardness

SM 2510 B 21st ED	**20048402**	**Conductivity by Probe**

Analyte Code	*Analyte*
1610	Conductivity

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SM 2540 B 21st ED	**20049201**	**Total Solids Dried at 103 - 105C**

Analyte Code	*Analyte*
1950	Residue-total

SM 2540 C 21st ED	**20050208**	**Total Dissolved Solids Dried at 180C**

Analyte Code	*Analyte*
1955	Residue-filterable (TDS)

SM 2540 D 21st ED	**20051007**	**Total Suspended Solids Dried at 103 - 105C**

Analyte Code	*Analyte*
1960	Residue-nonfilterable (TSS)

SM 2540 E 20th ED	**20051654**	**Total Volatile Solids**

Analyte Code	*Analyte*
1725	Total, fixed, and volatile residue

SM 2540 F 21st ED	**20052000**	**Settleable Solids**

Analyte Code	*Analyte*
1965	Residue-settleable

SM 4500-Cl C 20th ED	**20078802**	**Chlorine by Iodometric Method II**

Analyte Code	*Analyte*
1575	Chloride

SM 4500-Cl¯ F 20th ED	**20087201**	**Chloride by Ion Chromatography**

Analyte Code	*Analyte*
1945	Residual free chlorine

SM 4500-CN E 20th ED	**20092404**	**Cyanide by Colorimetric Determination**

Analyte Code	*Analyte*
1645	Total cyanide

SM 4500-CN F 20th ED	**20092802**	**Cyanide by Ion Selective Electrode**

Analyte Code	*Analyte*
1635	Cyanide
1640	Free cyanide
1645	Total cyanide

SM 4500-CN G 20th ED	**20093203**	**Cyanide Amenable to Chlorination after Distillation**

Analyte Code	*Analyte*
1510	Amenable cyanide

SM 4500-F¯ C 21st ED	**20102209**	**Fluoride by Ion-Selective Electrode Method**

Analyte Code	*Analyte*
1730	Fluoride

SM 4500-H+ B 21st ED	**20105004**	**pH Value by Electrometric Method .**

Analyte Code	*Analyte*

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Analyte Code	*Analyte*
1900	pH

SM 4500-NH3 C 18th ED **20023603** **Ammonia Nitrogen by Nesslerization**

Analyte Code	*Analyte*
1515	Ammonia as N

SM 4500-NH3 C 20th ED **20106405** **Ammonia Nitrogen by Titration**

Analyte Code	*Analyte*
1515	Ammonia as N

SM 4500-NH3 E 21st ED **20110003** **Ammonia by Ammonia-Selective Electrode Method Using Known Addition**

Analyte Code	*Analyte*
1515	Ammonia as N

SM 4500-NH3 F 18th ED **20023001** **Ammonia Nitrogen by Ion Selective Electrode**

Analyte Code	*Analyte*
1515	Ammonia as N

SM 4500-NH3 G 18th ED **20023205** **Ammonia Nitrogen by Ion Selective Electrode with Known Addition**

Analyte Code	*Analyte*
1515	Ammonia as N

SM 4500-NO_2^- B 18th ED **20024004** **Nitrite Nitrogen by Colorimetric Determination**

Analyte Code	*Analyte*
1840	Nitrite as N

SM 4500-NO_2^- B 21st ED **20112805** **Nitrite by Colorimetric Method**

Analyte Code	*Analyte*
1840	Nitrite as N

SM 4500-NO_3^- E 20th ED **20114403** **Nitrate Nitrogen by Cadmium Reduction Method**

Analyte Code	*Analyte*
1805	Nitrate
1810	Nitrate as N
1820	Nitrate-nitrite
1835	Nitrite
1840	Nitrite as N

SM 4500-NO_3^- E 21st ED **20114607** **Nitrate by Cadmium Reduction Method .**

Analyte Code	*Analyte*
1810	Nitrate as N
1820	Nitrate-nitrite

SM 4500-NO_3^- E minus SM 4500-NO_2^- B (calc.) 20th ED **20115202** **Nitrate Nitrogen by Cadmium Reduction Method (Calculated)**

Analyte Code	*Analyte*
1805	Nitrate

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SM 4500-Norg B 21st ED **20119000** **Nitrogen (Organic) by Macro-Kjeldahl Method**

Analyte Code	*Analyte*
1790	Kjeldahl nitrogen
1795	Kjeldahl nitrogen - total

SM 4500-Norg D 21st ED **20120267** **Nitrogen (Organic) by Block Digestion and Flow Injection Analysis**

Analyte Code	*Analyte*
1790	Kjeldahl nitrogen
1795	Kjeldahl nitrogen - total

SM 4500-O G 18th ED **20025405** **Dissolved Oxygen by Membrane Electrode Method**

Analyte Code	*Analyte*
1880	Oxygen, dissolved

SM 4500-O G 21st ED **20121408** **Oxygen by Membrane Electrode Method .**

Analyte Code	*Analyte*
1880	Oxygen, dissolved

SM 4500-P E 20th ED **20123802** **Phosphorus by Ascorbic Acid Reduction**

Analyte Code	*Analyte*
1870	Orthophosphate as P

SM 4500-P E 21st ED **20124009** **Phosphorus by Ascorbic Acid Method**

Analyte Code	*Analyte*
1870	Orthophosphate as P
1910	Phosphorus, total
1908	Total Phosphate

SM 4500-$S2^{-}$ D 21st ED **20125604** **Sulfide by Methylene Blue Method**

Analyte Code	*Analyte*
2005	Sulfide

SM 4500-$SO3^{-}$ B 21st ED **20130409** **Sulfite by Iodometric Method**

Analyte Code	*Analyte*
2015	Sulfite-SO3

SM 4500-$SO4^{-}$ E 20th ED **20132803** **Sulfate by Turbidity**

Analyte Code	*Analyte*
2000	Sulfate

SM 5210 B 21st ED **20135006** **Biochemical Oxygen Demand, 5-Day (BOD5)**

Analyte Code	*Analyte*
1530	Biochemical oxygen demand
1555	Carbonaceous BOD, CBOD

SM 5220 D 18th ED **20027809** **Chemical Oxygen Demand by Closed Reflux and Colorimetric Determination**

Analyte Code	*Analyte*
1565	Chemical oxygen demand

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SM 5310 B 20th ED **20137400** **Total Organic Carbon by Combustion Infra-red Method**

Analyte Code	*Analyte*
1710	Dissolved organic carbon (DOC)
2040	Total organic carbon

SM 5310 D 20th ED **20139406** **Total Organic Carbon by Wet Oxidation Method**

Analyte Code	*Analyte*
2040	Total organic carbon

SM 5520 B 20th ED **20141202** **Oil and Grease by Extraction and Gravimetric Determination**

Analyte Code	*Analyte*
1803	n-Hexane Extractable Material (O&G)
1860	Oil & Grease

SM 5540 C 20th ED **20144609** **Surfactants as MBAS**

Analyte Code	*Analyte*
2025	Surfactants - MBAS

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MATRIX : Solids

Reference	Code	Description
EPA 1010	**10116606**	**Pensky-Martens Closed-Cup Method for Determining Ignitability**

Analyte Code	*Analyte*
1780	Ignitability

Reference	Code	Description
EPA 1030	**10117201**	**Ignitability of Solids**

Analyte Code	*Analyte*
1780	Ignitability

Reference	Code	Description
EPA 1110	**10118000**	**Corrosivity Toward Steel**

Analyte Code	*Analyte*
1615	Corrosivity

Reference	Code	Description
EPA 1311	**10118806**	**Toxicity Characteristic Leaching Procedure**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 1312	**10119003**	**Synthetic Precipitation Leaching Procedure**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3005A	**10133207**	**Acid Digestion of waters for Total Recoverable or Dissolved Metals**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3010A	**10133605**	**Acid Digestion of Aqueous samples and Extracts for Total Metals**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3050B	**10135601**	**Acid Digestion of Sediments, Sludges, and soils**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3500B	**10137209**	**Organic Extraction and sample preparation**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3510C	**10138202**	**Separatory Funnel Liquid-liquid extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

Reference	Code	Description
EPA 3511	**10279808**	**Organic Compounds in Water by Microextraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

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EPA 3520C	**10139001**	**Continuous Liquid-liquid extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3540C	**10140202**	**Soxhlet Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3541	**10140406**	**Automated Soxhlet Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3545A	**10141001**	**Pressurized Fluid Extraction (PFE)**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3550B	**10141807**	**Ultrasonic Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3550C	**10142004**	**Ultrasonic Extraction**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 3630C	**10146802**	**Silica gel cleanup**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 413.2	**10078009**	**Oil and Grease - Spectrophotometric, Infrared.**

Analyte Code	*Analyte*
1860	Oil & Grease

EPA 418.1	**10079002**	**Petroleum Hydrocarbons - Spec. Infrared.**

Analyte Code	*Analyte*
2050	Total Petroleum Hydrocarbons (TPH)

EPA 5000	**10152600**	**Sample Preparation for Volatile Organics**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 5030B	**10153409**	**Purge and trap for aqueous samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 5030C	**10284603**	**Purge-and-Trap for Aqueous Samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

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EPA 5035 **10154004** **Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 5035A **10284807** **Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples**

Analyte Code	*Analyte*
8031	Extraction/Preparation

EPA 6010B **10155609** **ICP - AES**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1057	Gallium
1060	Gold
1760	Hardness (calc.)
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1175	Tin
1180	Titanium
1183	Tungsten
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 6010C **10155803** **ICP - AES**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium

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Analyte Code	*Analyte*
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1063	Indium
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1990	Silica as SiO2
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
2017	Sulfur
1165	Thallium
1175	Tin
1180	Titanium
1183	Tungsten
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 6020 **10156000** **Inductively Coupled Plasma-Mass Spectrometry**

Analyte Code	*Analyte*
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium
1030	Cadmium
1040	Chromium
1050	Cobalt
1055	Copper
1075	Lead
1100	Molybdenum
1105	Nickel
1140	Selenium
1150	Silver
1165	Thallium
1185	Vanadium
1190	Zinc

EPA 6020A **10156408** **Inductively Coupled Plasma-Mass Spectrometry**

Analyte Code	*Analyte*
1000	Aluminum
1005	Antimony
1010	Arsenic
1015	Barium
1020	Beryllium

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Analyte Code	*Analyte*
1023	Bismuth
1025	Boron
1030	Cadmium
1035	Calcium
1040	Chromium
1050	Cobalt
1055	Copper
1760	Hardness (calc.)
1070	Iron
1075	Lead
1080	Lithium
1085	Magnesium
1090	Manganese
1095	Mercury
1100	Molybdenum
1105	Nickel
1910	Phosphorus, total
1125	Potassium
1140	Selenium
1145	Silicon
1150	Silver
1155	Sodium
1160	Strontium
1165	Thallium
1170	Thorium
1175	Tin
1180	Titanium
3035	Uranium
1185	Vanadium
1190	Zinc
1192	Zirconium

EPA 6850 **10304606** **Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry**

Analyte Code	*Analyte*
1895	Perchlorate

EPA 7196A **10162400** **Chromium Hexavalent colorimetric**

Analyte Code	*Analyte*
1045	Chromium VI

EPA 7199 **10163005** **Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography**

Analyte Code	*Analyte*
1045	Chromium VI

EPA 7420 **10164406** **Lead by Flame Atomic Absorption**

Analyte Code	*Analyte*
1075	Lead

EPA 7470A **10165807** **Mercury in Liquid Waste by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*
1095	Mercury

EPA 7471A **10166208** **Mercury in Solid Waste by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*

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Analyte Code	*Analyte*
1095	Mercury

EPA 7471B **10166402** **Mercury by Cold Vapor Atomic Absorption**

Analyte Code	*Analyte*
1095	Mercury

EPA 8015B **10173601** **Non-halogenated organics using GC/FID**

Analyte Code	*Analyte*
9369	Diesel range organics (DRO)
4750	Ethanol
9408	Gasoline range organics (GRO)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
9488	Jet Fuel
9409	Kerosene
4930	Methanol
9410	Mineral Spirits
9499	Motor Oil
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
5055	n-Propanol
2050	Total Petroleum Hydrocarbons (TPH)
1935	Total recoverable petroleum hydrocarbons (TRPH)

EPA 8021B **10174808** **Aromatic and Halogenated Volatiles by GC with PID and/or ECD Purge & Trap**

Analyte Code	*Analyte*
4610	1,2-Dichlorobenzene
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4375	Benzene
4765	Ethylbenzene
5000	Methyl tert-butyl ether (MTBE)
5140	Toluene
5260	Xylene (total)

EPA 8081A **10178606** **Organochlorine Pesticides by GC/ECD**

Analyte Code	*Analyte*
8580	2,4'-DDD
8585	2,4'-DDE
8590	2,4'-DDT
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7005	Alachlor
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)
7065	Atrazine

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Analyte Code	*Analyte*
7115	beta-BHC (beta-Hexachlorocyclohexane)
7160	Butachlor
7185	Captafol
7250	Chlordane (tech.)
7260	Chlorobenzilate
7265	Chloroneb
7280	Chloropropylate
7300	Chlorpyrifos
7310	Chlorthalonil (Daconil)
7925	cis-Nonachlor
7965	cis-Permethrin
7340	Cyanazine
8550	Dacthal (DCPA)
7105	delta-BHC
7405	Diallate
4580	Dibromochloropropane
7430	Dichlone
7460	Dicofol
7470	Dieldrin
7473	Dimethazone (Clomazone)
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7575	Etridiazole
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6280	Hexachlorocyclohexanes
6285	Hexachlorocyclopentadiene
7725	Isodrin
7740	Kepone
7770	Malathion
7810	Methoxychlor
7825	Methyl parathion (Parathion, methyl)
7835	Metolachlor
7845	Metribuzin
7870	Mirex
7920	Nitrofen
3890	Oxychlordane
7955	Parathion, ethyl
6600	Pentachloronitrobenzene
7975	Permethrin (total)
7980	Perthane
8045	Propachlor (Ramrod)
6685	Safrole
8125	Simazine
8145	Strobane
8155	Sulfotepp
8210	Tetraethyl pyrophosphate (TEPP)
8250	Toxaphene (Chlorinated camphene)
7970	trans Permethrin
7910	trans-Nanochlor
8295	Trifluralin (Treflan)
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)

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EPA 8081B **10178800** **Organochlorine Pesticides by GC/ECD**

Analyte Code	*Analyte*
8580	2,4'-DDD
8585	2,4'-DDE
8590	2,4'-DDT
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
7005	Alachlor
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
7115	beta-BHC (beta-Hexachlorocyclohexane)
7185	Captafol
7250	Chlordane (tech.)
7260	Chlorobenzilate
7265	Chloroneb
7280	Chloropropylate
7300	Chlorpyrifos
7310	Chlorthalonil (Daconil)
7925	cis-Nonachlor
7965	cis-Permethrin
7340	Cyanazine
8550	Dacthal (DCPA)
7105	delta-BHC
7405	Diallate
7430	Dichlone
7460	Dicofol
7470	Dieldrin
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7575	Etridiazole
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7655	Halowax-1000
7660	Halowax-1001
7665	Halowax-1013
7670	Halowax-1014
7675	Halowax-1051
7680	Halowax-1099
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6280	Hexachlorocyclohexanes
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
7725	Isodrin
7740	Kepone
7810	Methoxychlor
7825	Methyl parathion (Parathion, methyl)
7870	Mirex
7920	Nitrofen
8290	o,o,o-Triethyl phosphorothioate
5554	Oxadiazon
3890	Oxychlordane

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Analyte Code	*Analyte*
7955	Parathion, ethyl
7957	PCNB
7975	Permethrin (total)
7980	Perthane
8045	Propachlor (Ramrod)
8060	Propazine
8145	Strobane
8250	Toxaphene (Chlorinated camphene)
7970	trans Permethrin
7910	trans-Nanochlor
8295	Trifluralin (Treflan)
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)

EPA 8082 **10179007** **Polychlorinated Biphenyls (PCBs) by GC/ECD**

Analyte Code	*Analyte*
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)

EPA 8082A **10179201** **Polychlorinated Biphenyls (PCBs) by GC/ECD**

Analyte Code	*Analyte*
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)

EPA 8141A **10182000** **Organophosphorous Pesticides by GC/NPD**

Analyte Code	*Analyte*
4310	Acetochlor
7005	Alachlor
7045	Anilazine
7065	Atrazine
7070	Azinphos-ethyl (Ethyl guthion)
7075	Azinphos-methyl (Guthion)
7125	Bolstar (Sulprofos)
7160	Butachlor
7175	Butylate
7205	Carbofuran (Furaden)
7220	Carbophenothion
7300	Chlorpyrifos
7305	Chlorpyrifos-methyl
7315	Coumaphos
7340	Cyanazine
7377	Deethyl atrazine (Desethyl atrazine)
7382	Deisopropyl atrazine
7390	Demeton

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Analyte Code	*Analyte*
7395	Demeton-o
7385	Demeton-s
7410	Diazinon
8605	Dichloroprop (Dichlorprop)
8610	Dichlorovos (DDVP, Dichlorvos)
7475	Dimethoate
8625	Disulfoton
7550	EPN
7555	EPTC (Eptam, s-ethyl-dipropyl thio carbamate)
7565	Ethion
7570	Ethoprop
7580	Famphur
7600	Fensulfothion
7605	Fenthion
7640	Fonophos (Fonofos)
7765	Linuron (Lorox)
7770	Malathion
7785	Merphos
7825	Methyl parathion (Parathion, methyl)
7835	Metolachlor
7845	Metribuzin
7850	Mevinphos
7880	Monocrotophos
7905	Naled
8290	o,o,o-Triethyl phosphorothioate
7955	Parathion, ethyl
7960	Pendimethalin\ (Penoxalin)
7985	Phorate
8000	Phosmet (Imidan)
8035	Prometon
8045	Propachlor (Ramrod)
8060	Propazine
8110	Ronnel
8125	Simazine
8155	Sulfotepp
8185	Terbufos
8200	Tetrachlorvinphos (Stirophos, Gardona) Z-isomer
8210	Tetraethyl pyrophosphate (TEPP)
8235	Thionazin (Zinophos)
8245	Tokuthion (Prothiophos)
8275	Trichloronate
8295	Trifluralin (Treflan)
8320	Vernolate

EPA 8151A **10183207** **Chlorinated Herbicides by GC/ECD**

Analyte Code	*Analyte*
8655	2,4,5-T
8545	2,4-D
8560	2,4-DB
8600	3,5-Dichlorobenzoic acid
6500	4-Nitrophenol
8505	Acifluorfen
8530	Bentazon
7135	Brominal (Bromoxynil)
8540	Chloramben
8550	Dacthal (DCPA)
8555	Dalapon
8595	Dicamba
8605	Dichloroprop (Dichlorprop)
8620	Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)

ORELAP Fields of Accreditation

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Eurofins Calscience, Inc.

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Garden Grove CA 92841-1427

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Analyte Code	*Analyte*
7650	Garlon (Triclopyr)
7775	MCPA
7780	MCPP
6605	Pentachlorophenol
8645	Picloram
8650	Silvex (2,4,5-TP)

EPA 8260B **10184802** **Volatile Organic Compounds by purge and trap GC/MS**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5165	1,1,2-Trichloroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
5215	1,3,5-Trimethylbenzene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4665	2,2-Dichloropropane
4410	2-Butanone (Methyl ethyl ketone, MEK)
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4860	2-Hexanone
5145	2-Methylaniline (o-Toluidine)
5020	2-Nitropropane
5050	2-Picoline (2-Methylpyridine)
4530	3-Chloropropionitrile
4540	4-Chlorotoluene
4995	4-Methyl-2-pentanone (MIBK)
4315	Acetone
4320	Acetonitrile
4325	Acrolein (Propenal)
4340	Acrylonitrile
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5635	Benzyl chloride
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4400	Bromoform
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4475	Chlorobenzene
4575	Chlorodibromomethane

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Analyte Code	*Analyte*
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4525	Chloroprene (2-Chloro-1,3-butadiene)
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4627	Dichlorofluoromethane (Freon 21)
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4755	Ethyl acetate
4810	Ethyl methacrylate
4765	Ethylbenzene
4795	Ethylene oxide
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4835	Hexachlorobutadiene
4840	Hexachloroethane
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4900	Isopropylbenzene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4975	Methylene chloride (Dichloromethane)
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4435	n-Butylbenzene
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5085	n-Propylamine
5090	n-Propylbenzene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
5095	Pyridine
4440	sec-Butylbenzene
5100	Styrene
4370	T-amylmethylether (TAME)
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5140	Toluene
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5225	Vinyl acetate
5235	Vinyl chloride
5260	Xylene (total)

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EPA 8260B SIM **10184904** **Volatile Organic Compounds by purge and trap GC/MS-SIM**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
5167	1,1,2-Trichlorofluoroethane
5172	1,1,2-Trifluoroethane
5171	1,1-Dichloro-1-fluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
4656	1,2-diethylbenzene
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4676	1,3-Diethylbenzene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4919	1-Chloro-1,1-difluoroethane
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4411	2-Chloro-1,1,1-trifluoroethane
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)

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Analyte Code	*Analyte*
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
6103	3,3'-dimethyl-1-butanol
4530	3-Chloropropionitrile
4534	3-Methylpentane
4536	4-Bromofluorobenzene
5712	4-Chloro-2-nitrophenol
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
9466	4-Nonylphenol diethoxylate
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor
4315	Acetone
4320	Acetonitrile
4323	Acetylene
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4577	Chlorodifluoromethane (Freon-22)
4485	Chloroethane (Ethyl chloride)
4486	Chlorofluoromethane
4505	Chloroform
4522	Chloropentafluoroethane
4525	Chloroprene (2-Chloro-1,3-butadiene)
4526	Chlorotrifluoroethene
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate

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Analyte Code	*Analyte*
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)

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Analyte Code	*Analyte*
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene
5095	Pyridine
6685	Safrole
9607	sec-Butyl Alcohol (2-Butanol)
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
9557	tert-butyl-formate
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
9574	Tetrahydrothiophene
5140	Toluene
4027	Total BTEX
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5237	Vinyl Fluoride
5260	Xylene (total)

EPA 8260C **10307003** **Volatile Organics: GC/MS (capillary column)**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
5167	1,1,2-Trichlorofluoroethane
5172	1,1,2-Trifluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene

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Analyte Code	*Analyte*
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5182	1,2,3-Trimethylbenzene
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
9318	1,3-Butadiene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
4919	1-Chloro-1,1-difluoroethane
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4411	2-Chloro-1,1,1-trifluoroethane
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4538	2-Ethyltoluene
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
4530	3-Chloropropionitrile
4531	3-Ethyltoluene (1-Methyl-3-ethylbenzene)
4534	3-Methylpentane
4536	4-Bromofluorobenzene
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
9466	4-Nonylphenol diethoxylate
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor

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Analyte Code	*Analyte*
4315	Acetone
4320	Acetonitrile
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4486	Chlorofluoromethane
4505	Chloroform
4522	Chloropentafluoroethane
4525	Chloroprene (2-Chloro-1,3-butadiene)
4526	Chlorotrifluoroethene
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate

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Analyte Code	*Analyte*
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5028	n-Pentane
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene

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Analyte Code	*Analyte*
5095	Pyridine
6685	Safrole
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
9574	Tetrahydrothiophene
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5237	Vinyl Fluoride
5260	Xylene (total)

EPA 8260C SIM **10307105** **Volatile Organic Compounds by GC/MS-SIM**

Analyte Code	*Analyte*
5105	1,1,1,2-Tetrachloroethane
5185	1,1,1-Trichloro-2,2,2-trifluoroethane
5190	1,1,1-Trichloro-2-propanone
5160	1,1,1-Trichloroethane
5110	1,1,2,2-Tetrachloroethane
5195	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
5165	1,1,2-Trichloroethane
5167	1,1,2-Trichlorofluoroethane
4630	1,1-Dichloroethane
4640	1,1-Dichloroethylene
4670	1,1-Dichloropropene
4710	1,2,3,4-Diepoxybutane
5150	1,2,3-Trichlorobenzene
5180	1,2,3-Trichloropropane
5155	1,2,4-Trichlorobenzene
5210	1,2,4-Trimethylbenzene
4570	1,2-Dibromo-3-chloropropane (DBCP)
4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
4697	1,2-Dichloro-1,1,2-trifluoroethane
4610	1,2-Dichlorobenzene
4635	1,2-Dichloroethane (Ethylene dichloride)
4655	1,2-Dichloropropane
6800	1,3,5-Trichlorobenzene
5215	1,3,5-Trimethylbenzene
4690	1,3-Dichloro-2-propanol
4615	1,3-Dichlorobenzene
4660	1,3-Dichloropropane
4675	1,3-Dichloropropene
4620	1,4-Dichlorobenzene
4622	1,4-Difluorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)

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Analyte Code	*Analyte*
4480	1-Chlorobutane
4510	1-Chlorohexane
4830	1-Heptene
6380	1-Methylnaphthalene
5220	2,2,4-Trimethylpentane
5222	2,2-Dichloro-1,1,1-trifluoroethane (Freon 123)
4665	2,2-Dichloropropane
6830	2,3,6-Trichlorophenol (4C)
4668	2,3-Dichloropropene
4410	2-Butanone (Methyl ethyl ketone, MEK)
4490	2-Chloroethanol
4500	2-Chloroethyl vinyl ether
4535	2-Chlorotoluene
4537	2-Ethylhexanol (2-Ethyl-1-hexanol)
4860	2-Hexanone (MBK)
4865	2-Hydroxypropionitrile
4935	2-Methoxyethanol (Methyl cellosolve)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
4941	2-Methylpentane (Isohexane)
5020	2-Nitropropane
5045	2-Pentanone
5050	2-Picoline (2-Methylpyridine)
6103	3,3'-dimethyl-1-butanol
4530	3-Chloropropionitrile
4534	3-Methylpentane
4536	4-Bromofluorobenzene
5712	4-Chloro-2-nitrophenol
4540	4-Chlorotoluene
4910	4-Isopropyltoluene (p-Cymene)
4995	4-Methyl-2-pentanone (MIBK)
4300	Acetaldehyde
4305	Acetamide
4310	Acetochlor
4315	Acetone
4320	Acetonitrile
4323	Acetylene
4325	Acrolein (Propenal)
4330	Acrylamide
4335	Acrylic acid
4340	Acrylonitrile
4345	Adsorbable organic halogens (AOX)
4350	Allyl alcohol
4355	Allyl chloride (3-Chloropropene)
4375	Benzene
5630	Benzyl alcohol
5635	Benzyl chloride
5075	beta-Propiolactone
4495	bis(2-Chloroethyl) sulfide
5780	bis(2-Chloroisopropyl) ether
4515	bis(Chloromethyl)ether
4380	Bromoacetone
4385	Bromobenzene
4390	Bromochloromethane
4395	Bromodichloromethane
4397	Bromoethane (Ethyl Bromide)
4400	Bromoform
4430	Butylaldehyde (Butanal)
4450	Carbon disulfide
4455	Carbon tetrachloride
4460	Chloral hydrate

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Analyte Code	*Analyte*
4465	Chloroacetaldehyde
4470	Chloroacetonitrile
4475	Chlorobenzene
4575	Chlorodibromomethane
4485	Chloroethane (Ethyl chloride)
4505	Chloroform
4525	Chloroprene (2-Chloro-1,3-butadiene)
4705	cis & trans-1,2-Dichloroethene
4645	cis-1,2-Dichloroethylene
4680	cis-1,3-Dichloropropene
4600	cis-1,4-Dichloro-2-butene
4545	Crotonaldehyde
4550	Cycloate
4555	Cyclohexane
4560	Cyclohexanone
4565	Decanal
4580	Dibromochloropropane
4590	Dibromofluoromethane
4595	Dibromomethane (Methylene bromide)
4625	Dichlorodifluoromethane (Freon-12)
4627	Dichlorofluoromethane (Freon 21)
4653	Dicyclopentadiene
4725	Diethyl ether
4715	Diethylamine
4720	Diethylene glycol (2,2-Oxybisethanol)
9375	Di-isopropylether (DIPE)
4729	Dimethyl disulfide
4730	Dimethyl sulfoxide
4745	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
4750	Ethanol
4755	Ethyl acetate
4760	Ethyl acrylate
4810	Ethyl methacrylate
4765	Ethylbenzene
4785	Ethylene glycol
4795	Ethylene oxide
4800	Ethylene thiourea
4790	Ethyleneimine
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
4771	Fluorobenzene
4772	Fluoromethane (Freon 41)
4815	Formaldehyde
9408	Gasoline range organics (GRO)
4820	Heptanal
4835	Hexachlorobutadiene
4840	Hexachloroethane
3825	Hexanaldehyde (Hexanal)
4870	Iodomethane (Methyl iodide)
4875	Isobutyl alcohol (2-Methyl-1-propanol)
4880	Isobutyraldehyde
4890	Isopropyl acetate
4895	Isopropyl alcohol (2-Propanol, Isopropanol)
4900	Isopropylbenzene
5240	m+p-xylene
4920	Malononitrile
4925	Methacrylonitrile
4930	Methanol
4940	Methyl acetate
4945	Methyl acrylate
4950	Methyl bromide (Bromomethane)
4960	Methyl chloride (Chloromethane)

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Analyte Code	*Analyte*
4980	Methyl formate
4990	Methyl methacrylate
5000	Methyl tert-butyl ether (MTBE)
4965	Methylcyclohexane
4966	Methylcyclopentane
4975	Methylene chloride (Dichloromethane)
5125	m-Tolualdehyde (1,3-Tolualdehyde)
5245	m-Xylene
5010	n, n-Dimethyl formamide
4360	n-Amyl acetate
4365	n-Amyl alcohol
5005	Naphthalene
4425	n-Butyl alcohol (1-Butanol, n-Butanol)
4415	n-Butyl-acetate
4435	n-Butylbenzene
4825	n-Heptane
4855	n-Hexane
5015	Nitrobenzene
5025	n-Nitroso-di-n-butylamine
5055	n-Propanol
5085	n-Propylamine
5090	n-Propylbenzene
6755	o-Tolualdehyde (1,2-Tolualdehyde)
5250	o-Xylene
5030	Paraldehyde
5035	Pentachloroethane
5040	Pentafluorobenzene
5070	Propargyl alcohol
5080	Propionitrile (Ethyl cyanide)
9579	Propylene oxide
5255	p-Xylene
5095	Pyridine
6685	Safrole
4440	sec-Butylbenzene
4442	S-Methyl thioacetate (S-Methyl etanethioate)
5100	Styrene
4370	T-amylmethylether (TAME)
4368	tert-amyl alcohol
4420	tert-Butyl alcohol
4445	tert-Butylbenzene
9557	tert-butyl-formate
5115	Tetrachloroethylene (Perchloroethylene)
5120	Tetrahydrofuran (THF)
5140	Toluene
5205	Total trihalomethanes
4700	trans-1,2-Dichloroethylene
4685	trans-1,3-Dichloropropylene
4605	trans-1,4-Dichloro-2-butene
5170	Trichloroethene (Trichloroethylene)
5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)
5200	Triethylamine
5225	Vinyl acetate
5230	Vinyl bromide (Bromoethane)
5235	Vinyl chloride
5260	Xylene (total)

EPA 8270C **10185805** **Semivolatile Organic compounds by GC/MS**

Analyte Code	*Analyte*
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene

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Analyte Code	*Analyte*
4610	1,2-Dichlorobenzene
6155	1,2-Dinitrobenzene
6221	1,2-Diphenylhydrazine
6800	1,3,5-Trichlorobenzene
4615	1,3-Dichlorobenzene
6160	1,3-Dinitrobenzene (1,3-DNB)
4620	1,4-Dichlorobenzene
6165	1,4-Dinitrobenzene
6420	1,4-Naphthoquinone
6630	1,4-Phenylenediamine
5520	1-Acetyl-2-thiourea
5790	1-Chloronaphthalene
6425	1-Naphthylamine
6735	2,3,4,6-Tetrachlorophenol
6835	2,4,5-Trichlorophenol
6840	2,4,6-Trichlorophenol
5880	2,4-Diaminotoluene
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
9636	2,4-Toluene diisocyanate
6005	2,6-Dichlorophenol
6190	2,6-Dinitrotoluene (2,6-DNT)
5515	2-Acetylaminofluorene
5795	2-Chloronaphthalene
5800	2-Chlorophenol
5865	2-Cyclohexyl-4,6-dinitrophenol
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6430	2-Naphthylamine
6460	2-Nitroaniline
6490	2-Nitrophenol
5050	2-Picoline (2-Methylpyridine)
6100	3,3'-Dimethoxybenzidine
6120	3,3'-Dimethylbenzidine
5740	3-Chloroaniline
6355	3-Methylcholanthrene
6405	3-Methylphenol (m-Cresol)
6465	3-Nitroaniline
5540	4-Aminobiphenyl
5660	4-Bromophenyl phenyl ether
5700	4-Chloro-3-methylphenol
5745	4-Chloroaniline
5825	4-Chlorophenyl phenylether
6105	4-Dimethyl aminoazobenzene
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
6570	5-Nitro-o-toluidine
6115	7,12-Dimethylbenz(a) anthracene
6125	a-a-Dimethylphenethylamine
5500	Acenaphthene
5505	Acenaphthylene
5510	Acetophenone
5545	Aniline
5555	Anthracene
5560	Aramite
5595	Benzidine

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Analyte Code	*Analyte*
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5590	Benzo(g,h,i)perylene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5610	Benzoic acid
5630	Benzyl alcohol
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
5670	Butyl benzyl phthalate
5680	Carbazole
5855	Chrysene
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5900	Dibenz(a, j) acridine
5895	Dibenz(a,h) anthracene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
6070	Diethyl phthalate
6080	Diethyl sulfate
6075	Diethylstilbestrol
6090	Dihydrosafrole
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
6205	Diphenylamine
6250	Ethyl carbamate (Urethane)
6260	Ethyl methanesulfonate
6265	Fluoranthene
6270	Fluorene
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
6290	Hexachlorophene
6295	Hexachloropropene
6315	Indeno(1,2,3-cd) pyrene
6320	Isophorone
6325	Isosafrole
6335	Maleic anhydride
6375	Methyl methanesulfonate
5005	Naphthalene
6450	Nicotine
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6555	n-Nitrosomorpholine
6560	n-Nitrosopiperidine
6565	n-Nitrosopyrrolidine
5620	p-Benzoquinone (Quinone)
6590	Pentachlorobenzene
6600	Pentachloronitrobenzene
6605	Pentachlorophenol
6610	Phenacetin
6615	Phenanthrene
6625	Phenol
6640	Phthalic anhydride

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Analyte Code	*Analyte*
6650	Pronamide (Kerb)
6660	Propylthiouracil
6665	Pyrene
5095	Pyridine
6680	Resorcinol
6685	Safrole
6695	Strychnine
6750	Thiophenol (Benzenethiol)

EPA 8270C SIM **10242407** **Semivolatile Organic compounds by GC/MS Selective Ion Monitoring**

Analyte Code	*Analyte*
6703	1,1'-Biphenyl (BZ-0)
6715	1,2,4,5-Tetrachlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6380	1-Methylnaphthalene
5795	2-Chloronaphthalene
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6412	3 & 4 Methylphenol
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
5500	Acenaphthene
5505	Acenaphthylene
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
5555	Anthracene
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
7115	beta-BHC (beta-Hexachlorocyclohexane)
5670	Butyl benzyl phthalate
5680	Carbazole
7250	Chlordane (tech.)
5855	Chrysene
7105	delta-BHC
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5895	Dibenz(a,h) anthracene
5905	Dibenzofuran
5910	Dibenzothiophene
7470	Dieldrin
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
6265	Fluoranthene

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Analyte Code	*Analyte*
6270	Fluorene
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
4840	Hexachloroethane
6312	Indene
6315	Indeno(1,2,3-cd) pyrene
7810	Methoxychlor
5005	Naphthalene
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6555	n-Nitrosomorpholine
6590	Pentachlorobenzene
6605	Pentachlorophenol
6608	Perylene
6615	Phenanthrene
6665	Pyrene
5095	Pyridine
6670	Quinoline

EPA 8270D **10186002** **Semivolatile Organic compounds by GC/MS**

Analyte Code	*Analyte*
6705	1,2,3,4-Tetrachlorobenzene
6707	1,2,3,4-Tetrahydronaphthalene
6710	1,2,3,5-Tetrachlorobenzene
5150	1,2,3-Trichlorobenzene
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6155	1,2-Dinitrobenzene
6221	1,2-Diphenylhydrazine
9564	1,2-Phenylenediamine (o-Phenylenediamine)
6800	1,3,5-Trichlorobenzene
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
4615	1,3-Dichlorobenzene
6160	1,3-Dinitrobenzene (1,3-DNB)
4620	1,4-Dichlorobenzene
6165	1,4-Dinitrobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6420	1,4-Naphthoquinone
6630	1,4-Phenylenediamine
9330	1-Chloro-4-nitrobenzene
5790	1-Chloronaphthalene
5792	1-Chloropropane
6380	1-Methylnaphthalene
9501	1-Methylphenanthrene
6425	1-Naphthylamine
187	1-Phenoxy-2-propanol
5754	1-Phenoxy-2-propanol
4659	2,2-Oxybis(1-chloropropane)
6730	2,3,4,5-Tetrachlorophenol
6735	2,3,4,6-Tetrachlorophenol
6740	2,3,5,6-Tetrachlorophenol

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Analyte Code	*Analyte*
5983	2,3-Dichlorophenol
6014	2,3-Dinitrotoluene
6017	2,4 & 2,6-Toluene Diamine
6790	2,4,5-Trichloroaniline
6835	2,4,5-Trichlorophenol
6795	2,4,6-Trichloroaniline
6840	2,4,6-Trichlorophenol
6890	2,4,6-Trinitrobenzene
5930	2,4-Dichloro-6-methylphenol
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
5992	2,5-Dichlorophenol
6180	2,5-Dinitrophenol
6005	2,6-Dichlorophenol
6190	2,6-Dinitrotoluene (2,6-DNT)
5515	2-Acetylaminofluorene
5735	2-Chloroaniline
5795	2-Chloronaphthalene
5800	2-Chlorophenol
5865	2-Cyclohexyl-4,6-dinitrophenol
5866	2-Ethoxyethanol (cellosolve)
5867	2-Fluorobiphenyl
5868	2-Methoxyphenol (Guaiacol)
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6430	2-Naphthylamine
6460	2-Nitroaniline
6490	2-Nitrophenol
9507	2-Nitrotoluene
5050	2-Picoline (2-Methylpyridine)
6692	2-Terphenyl
6412	3 & 4 Methylphenol
5945	3,3'-Dichlorobenzidine
6100	3,3'-Dimethoxybenzidine
6120	3,3'-Dimethylbenzidine
6815	3,4,5-Trichloroguaiacol
5940	3,4-Dichloroaniline
5995	3,4-Dichloronitrobenzene
5997	3,4-Dichlorophenol
9364	3,4-Methylenedioxyamphetamine (MDA)
5527	3-beta-Coprostanol
5740	3-Chloroaniline
4742	3-Chlorophenol
4530	3-Chloropropionitrile
6355	3-Methylcholanthrene
6405	3-Methylphenol (m-Cresol)
6465	3-Nitroaniline
9510	3-Nitrotoluene
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
6365	4,4-Methylenebis(2-chloroaniline)
6825	4,5,6-Trichloroguaiacol
6827	4,5-Dichloro-2-methoxyphenol (4,5-Dichloroguaiacol)
5540	4-Aminobiphenyl
5660	4-Bromophenyl phenyl ether (BDE-3)
5853	4-Chloro-2-methylphenol

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Analyte Code	*Analyte*
5700	4-Chloro-3-methylphenol
5745	4-Chloroaniline
5805	4-Chlorophenol
5825	4-Chlorophenyl phenylether
6105	4-Dimethyl aminoazobenzene
4910	4-Isopropyltoluene (p-Cymene)
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
6510	4-Nitroquinoline 1-oxide
9513	4-Nitrotoluene
6513	4-Nonylphenol
6516	4-tert-Butylphenol
6570	5-Nitro-o-toluidine
6572	6-Chloro-3-methylphenol
6112	6-Methylchrysene
6115	7,12-Dimethylbenz(a) anthracene
9417	7h-Dibenzo(c, g) carbazole
6125	a-a-Dimethylphenethylamine
5500	Acenaphthene
5505	Acenaphthylene
4310	Acetochlor
5510	Acetophenone
4330	Acrylamide
5445	Aflatoxin B1
5450	Aflatoxin B2
5455	Aflatoxin G1
5460	Aflatoxin G2
7005	Alachlor
7010	Aldicarb (Temik)
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
4357	alpha-Methylstyrene
6700	alpha-Terpineol
9367	Amphetamine
5545	Aniline
5555	Anthracene
5560	Aramite
8880	Aroclor-1016 (PCB-1016)
8885	Aroclor-1221 (PCB-1221)
8890	Aroclor-1232 (PCB-1232)
8895	Aroclor-1242 (PCB-1242)
8900	Aroclor-1248 (PCB-1248)
8905	Aroclor-1254 (PCB-1254)
8910	Aroclor-1260 (PCB-1260)
8912	Aroclor-1262 (PCB-1262)
8913	Aroclor-1268 (PCB-1268)
7055	Asulam
7065	Atrazine
7070	Azinphos-ethyl (Ethyl guthion)
7075	Azinphos-methyl (Guthion)
5562	Azobenzene
5565	Benzal chloride
5570	Benzaldehyde
5567	Benzenethiol (Phenylmercaptan)
5595	Benzidine
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene

ORELAP Fields of Accreditation

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Analyte Code	*Analyte*
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5610	Benzoic acid
5625	Benzotrichloride
5630	Benzyl alcohol
5635	Benzyl chloride
7115	beta-BHC (beta-Hexachlorocyclohexane)
6437	beta-Pinene
6438	beta-Sitosterol
5640	Biphenyl
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
6062	bis(2-Ethylhexyl)adipate
4515	bis(Chloromethyl)ether
7125	Bolstar (Sulprofos)
7160	Butachlor
5670	Butyl benzyl phthalate
5671	Butyl diphenyl Phosphate
7175	Butylate
5673	Butylated Hydroxy Toluene (BHT)
5675	Caffeine
7180	Caprolactam
5680	Carbazole
7205	Carbofuran (Furaden)
7210	Carbofuran phenol
7220	Carbophenothion
7255	Chlorfenvinphos
7260	Chlorobenzilate
7300	Chlorpyrifos
5683	Cholesterol
5855	Chrysene
8906	Coelution - 3-Chlorophenol + 4-Chlorophenol
6414	Coelution - 3-Phenoxyphenol + 4-Phenoxyphenol
7315	Coumaphos
5862	Cresols, Total
7330	Crotoxyphos
7340	Cyanazine
7377	Deethyl atrazine (Desethyl atrazine)
7382	Deisopropyl atrazine
7105	delta-BHC
7390	Demeton
7395	Demeton-o
7385	Demeton-s
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
7405	Diallate
7410	Diazinon
9354	Dibenz(a, h) acridine
5900	Dibenz(a, j) acridine
5895	Dibenz(a,h) anthracene
9348	Dibenzo(a, h) pyrene
9351	Dibenzo(a, i) pyrene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
5910	Dibenzothiophene
5912	Dibutyl phenyl Phospahate
4625	Dichlorodifluoromethane (Freon-12)
8610	Dichlorovos (DDVP, Dichlorvos)
7460	Dicofol
7465	Dicrotophos

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Analyte Code	*Analyte*
7470	Dieldrin
9369	Diesel range organics (DRO)
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
7473	Dimethazone (Clomazone)
7474	Dimetheneamid
7475	Dimethoate
6135	Dimethyl phthalate
6137	Dimethyl terphthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
8620	Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)
7495	Dioxathion
6210	Diphenyl ether (Diphenyl Oxide)
6205	Diphenylamine
8625	Disulfoton
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
7550	EPN
7555	EPTC (Eptam, s-ethyl-dipropyl thio carbamate)
7560	Ethalfluralin (Sonalan)
7565	Ethion
7570	Ethoprop
6260	Ethyl methanesulfonate
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
7580	Famphur
7600	Fensulfothion
7605	Fenthion
7625	Fluchloralin
6265	Fluoranthene
6270	Fluorene
7640	Fonophos (Fonofos)
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
6285	Hexachlorocyclopentadiene
4840	Hexachloroethane
6290	Hexachlorophene
6295	Hexachloropropene
6312	Indene
6315	Indeno(1,2,3-cd) pyrene
7725	Isodrin
7727	Isofenphos
6320	Isophorone
6321	Isoquinoline
6325	Isosafrole
7740	Kepone
7770	Malathion
7785	Merphos
7316	Methadone
6342	Methamphetamine
6345	Methapyrilene
7810	Methoxychlor
6375	Methyl methanesulfonate

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Analyte Code	*Analyte*
7825	Methyl parathion (Parathion, methyl)
6377	Methyl styrene
9598	Methyldiethanolamine (MDEA)
9599	Methylenedioxymethamphetamine (MDMA)
7835	Metolachlor
7845	Metribuzin
7850	Mevinphos
7880	Monocrotophos
5010	n, n-Dimethyl formamide
6443	n, n-Dimethylacetamide
7905	Naled
5005	Naphthalene
5875	n-Decane
6300	n-Hexadecane
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6555	n-Nitrosomorpholine
6560	n-Nitrosopiperidine
6565	n-Nitrosopyrrolidine
6580	n-Octadecane
6745	n-Tetradecane
8290	o,o,o-Triethyl phosphorothioate
5553	Octachlorostyrene
3960	o-Phenylphenol
7955	Parathion, ethyl
9537	Pebulate
7960	Pendimethalin\ (Penoxalin)
5872	Pentabromodiphenyl Ether
6590	Pentachlorobenzene
5035	Pentachloroethane
6600	Pentachloronitrobenzene
6605	Pentachlorophenol
6608	Perylene
6610	Phenacetin
6615	Phenanthrene
6625	Phenol
7985	Phorate
8000	Phosmet (Imidan)
6635	Phthalic acid
6640	Phthalic anhydride
9663	p-Phenylenediamine
8035	Prometon
6650	Pronamide (Kerb)
8045	Propachlor (Ramrod)
8060	Propazine
6760	p-Tolualdehyde (1,4-Tolualdehyde)
6665	Pyrene
5095	Pyridine
6670	Quinoline
6683	Retene
8110	Ronnel
6685	Safrole
8125	Simazine
8155	Sulfotepp
8185	Terbufos
6725	Tetrachloroguaiacol

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Analyte Code	*Analyte*
8200	Tetrachlorvinphos (Stirophos, Gardona) Z-isomer
8210	Tetraethyl pyrophosphate (TEPP)
1210	Tetraethyl Tin
8235	Thionazin (Zinophos)
8245	Tokuthion (Prothiophos)
8260	Triallate
8262	Tributyl phosphate
8275	Trichloronate
5200	Triethylamine
8295	Trifluralin (Treflan)
8282	Triphenyl phosphate
8310	tris-(2,3-Dibromopropyl) phosphate (tris-BP)
8320	Vernolate

EPA 8270D SIM **10242509** **Semivolatile Organic compounds by GC/MS Selective Ion Monitoring**

Analyte Code	*Analyte*
6715	1,2,4,5-Tetrachlorobenzene
5155	1,2,4-Trichlorobenzene
4610	1,2-Dichlorobenzene
6221	1,2-Diphenylhydrazine
4615	1,3-Dichlorobenzene
4620	1,4-Dichlorobenzene
4735	1,4-Dioxane (1,4- Diethyleneoxide)
6380	1-Methylnaphthalene
9501	1-Methylphenanthrene
6852	2,3,5-Trimethylnaphthalene
6835	2,4,5-Trichlorophenol
6840	2,4,6-Trichlorophenol
5930	2,4-Dichloro-6-methylphenol
6000	2,4-Dichlorophenol
6130	2,4-Dimethylphenol
6175	2,4-Dinitrophenol
6185	2,4-Dinitrotoluene (2,4-DNT)
6188	2,6-Dimethylnaphthalene
6190	2,6-Dinitrotoluene (2,6-DNT)
5795	2-Chloronaphthalene
5800	2-Chlorophenol
6360	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)
5145	2-Methylaniline (o-Toluidine)
6385	2-Methylnaphthalene
6400	2-Methylphenol (o-Cresol)
6460	2-Nitroaniline
6490	2-Nitrophenol
6412	3 & 4 Methylphenol
7355	4,4'-DDD
7360	4,4'-DDE
7365	4,4'-DDT
5660	4-Bromophenyl phenyl ether (BDE-3)
5700	4-Chloro-3-methylphenol
5825	4-Chlorophenyl phenylether
6410	4-Methylphenol (p-Cresol)
6470	4-Nitroaniline
6500	4-Nitrophenol
5500	Acenaphthene
5505	Acenaphthylene
7025	Aldrin
7110	alpha-BHC (alpha-Hexachlorocyclohexane)
7240	alpha-Chlordane
5555	Anthracene
5595	Benzidine

ORELAP Fields of Accreditation

ORELAP ID: CA300001
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Analyte Code	*Analyte*
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5630	Benzyl alcohol
7115	beta-BHC (beta-Hexachlorocyclohexane)
5640	Biphenyl
5760	bis(2-Chloroethoxy)methane
5765	bis(2-Chloroethyl) ether
5780	bis(2-Chloroisopropyl) ether
5670	Butyl benzyl phthalate
1201	Butyltin trichloride
5680	Carbazole
5855	Chrysene
7105	delta-BHC
6065	Di(2-ethylhexyl) phthalate (bis(2-Ethylhexyl)phthalate, DEHP)
5895	Dibenz(a,h) anthracene
5905	Dibenzofuran
5910	Dibenzothiophene
5913	Dibutyltin
1202	Dibutyltin dichloride
7470	Dieldrin
6070	Diethyl phthalate
9375	Di-isopropylether (DIPE)
6135	Dimethyl phthalate
5925	Di-n-butyl phthalate
6200	Di-n-octyl phthalate
7510	Endosulfan I
7515	Endosulfan II
7520	Endosulfan sulfate
7540	Endrin
7530	Endrin aldehyde
7535	Endrin ketone
4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
6265	Fluoranthene
6270	Fluorene
7120	gamma-BHC (Lindane, gamma-HexachlorocyclohexanE)
7245	gamma-Chlordane
7685	Heptachlor
7690	Heptachlor epoxide
6275	Hexachlorobenzene
4835	Hexachlorobutadiene
4840	Hexachloroethane
6315	Indeno(1,2,3-cd) pyrene
6320	Isophorone
7810	Methoxychlor
1206	Monobutyltin
5005	Naphthalene
5015	Nitrobenzene
6525	n-Nitrosodiethylamine
6530	n-Nitrosodimethylamine
5025	n-Nitroso-di-n-butylamine
6545	n-Nitrosodi-n-propylamine
6535	n-Nitrosodiphenylamine
6550	n-Nitrosomethylethalamine
6590	Pentachlorobenzene
6605	Pentachlorophenol
6608	Perylene

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Analyte Code	*Analyte*
6615	Phenanthrene
6625	Phenol
6665	Pyrene
5095	Pyridine
1209	Tetrabutyltin
1213	Tributyltin
1203	Tributyltin chloride

EPA 8310 **10187607** **Polynuclear Aromatic Hydrocarbons by HPLC/UV-VIS**

Analyte Code	*Analyte*
6380	1-Methylnaphthalene
6385	2-Methylnaphthalene
5500	Acenaphthene
5505	Acenaphthylene
5555	Anthracene
5575	Benzo(a)anthracene
5580	Benzo(a)pyrene
5605	Benzo(e)pyrene
5590	Benzo(g,h,i)perylene
9309	Benzo(j)fluoranthene
5600	Benzo(k)fluoranthene
5585	Benzo[b]fluoranthene
5855	Chrysene
5895	Dibenz(a,h) anthracene
9348	Dibenzo(a, h) pyrene
9351	Dibenzo(a, i) pyrene
5890	Dibenzo(a,e) pyrene
5905	Dibenzofuran
6265	Fluoranthene
6270	Fluorene
6315	Indeno(1,2,3-cd) pyrene
5005	Naphthalene
6615	Phenanthrene
6665	Pyrene

EPA 8330 **10189807** **Nitroaromatics and Nitramines by HPLC/UV-VIS**

Analyte Code	*Analyte*
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
6160	1,3-Dinitrobenzene (1,3-DNB)
9651	2,4,6-Trinitrotoluene (2,4,6-TNT)
6185	2,4-Dinitrotoluene (2,4-DNT)
6190	2,6-Dinitrotoluene (2,6-DNT)
9303	2-Amino-4,6-dinitrotoluene (2-am-dnt)
6462	2-Nitroguanidine
9507	2-Nitrotoluene
9510	3-Nitrotoluene
9306	4-Amino-2,6-dinitrotoluene (4-am-dnt)
9513	4-Nitrotoluene
6415	Methyl-2,4,6-trinitrophenylnitramine (tetryl)
5015	Nitrobenzene
6485	Nitroglycerin
9522	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
9558	Pentaerythritoltetranitrate (PETN)
9432	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)

EPA 8330A **10190008** **Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)**

Analyte Code	*Analyte*

ORELAP Fields of Accreditation

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Analyte Code	*Analyte*
6885	1,3,5-Trinitrobenzene (1,3,5-TNB)
6160	1,3-Dinitrobenzene (1,3-DNB)
9651	2,4,6-Trinitrotoluene (2,4,6-TNT)
5882	2,4-diamino-6-nitrotoluene
6185	2,4-Dinitrotoluene (2,4-DNT)
6181	2,6-diamino-4-nitrotoluene
6190	2,6-Dinitrotoluene (2,6-DNT)
9303	2-Amino-4,6-dinitrotoluene (2-am-dnt)
9507	2-Nitrotoluene
9510	3-Nitrotoluene
9306	4-Amino-2,6-dinitrotoluene (4-am-dnt)
9513	4-Nitrotoluene
7046	Ammonium Picrate
6415	Methyl-2,4,6-trinitrophenylnitramine (tetryl)
9418	MNX
5015	Nitrobenzene
6485	Nitroglycerin
9522	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
9558	Pentaerythritoltetranitrate (PETN)
1899	Picric Acid (2,4,6-Trinitrophenol)
9432	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)

EPA 9014 **10193803** **Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide**

Analyte Code	*Analyte*
1635	Cyanide
1645	Total cyanide

EPA 9034 **10196006** **Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides**

Analyte Code	*Analyte*
2005	Sulfide

EPA 9040B **10197203** **pH Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 9040C **10244403** **pH Electrometric Measurement**

Analyte Code	*Analyte*
1900	pH

EPA 9045C **10198400** **Soil and Waste pH**

Analyte Code	*Analyte*
1900	pH

EPA 9056 **10199005** **Determination of Inorganic Anions by Ion Chromatography**

Analyte Code	*Analyte*
1540	Bromide
1575	Chloride
1730	Fluoride
1805	Nitrate
1835	Nitrite
1870	Orthophosphate as P
2000	Sulfate
1825	Total nitrate+nitrite

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EPA 9214 **10206403** **Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode**

Analyte Code	*Analyte*
1730	Fluoride

EPA SW-846 Chapter 7.3 **10245702** **Characteristic Determination - Reactivity**

Analyte Code	*Analyte*
1923	Reactive Cyanide
1925	Reactive sulfide

NWTPH-Dx **90018409** **Oregon DEQ TPH Diesel Range**

Analyte Code	*Analyte*
9369	Diesel range organics (DRO)
9488	Jet Fuel
9499	Motor Oil
9506	Residual Range Organics (RRO)

NWTPH-Gx **90018603** **Oregon DEQ TPH Gasoline Range Organics by GC/FID-PID Purge & Trap**

Analyte Code	*Analyte*
9408	Gasoline range organics (GRO)

Polisini & Miller (CDFG 1988) **970** **Static Acute Bioassay Procedures for Hazardous Waste Samples**

Analyte Code	*Analyte*
800	Fathead Minnow (P. promelas)

California State
Environmental Laboratory Accreditation Program

CALIFORNIA
Water Boards

Edmund G. Brown Jr.
Governor

Matthew Rodriquez
Secretary for
Environmental Protection

State Water Resources Control Board

September 28, 2016

Elizabeth Winger
Eurofins Calscience, Inc.
7440 Lincoln Way
Garden Grove, CA 92841-1427

Dear Elizabeth Winger: Certificate No. 2944

This notice advises that the laboratory named above has been certified as an environmental testing laboratory pursuant to the provisions of the Health and Safety Code (HSC), Division 101, Part 1, Chapter 4, Section 100825, *et seq.*

The Fields of Testing for which this laboratory has been certified are indicated on the enclosed "Fields of Testing" list. The certificate shall remain in effect until **September 30, 2018** unless it is revoked. This certificate is subject to an annual fee as determined by HSC 100860.1(a).

The application for renewal of this certificate must be received 90 days prior to the expiration date to remain in force according to HSC 100845(a). You must submit annual Proficiency Testing results before the due date of your annual fee to remain in compliance.

Any change in laboratory location or alteration to laboratory structure that could adversely affect quality of analysis in certified methods require notification prior to the change. Notification is also required for a transfer in ownership or appointment of new laboratory director within 30 days of the change (HSC, Section 100845(b) and (d)).

Your continued cooperation with the above requirements is essential for maintaining the high quality of the data produced by environmental laboratories certified by the State of California.

For general inquiries, please contact our office at the phone number or email address listed below. For specific concerns regarding your application, please call (916) 341-5175 or email Christine.Sotelo@waterboards.ca.gov.

Sincerely,

Christine Sotelo, Chief
Environmental Laboratory Accreditation Program

Enclosure

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

CALIFORNIA STATE

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

CERTIFICATE OF ENVIRONMENTAL ACCREDITATION

Is hereby granted to

Eurofins Calscience, Inc.

7440 Lincoln Way

Garden Grove, CA 92841-1427

Scope of the certificate is limited to the
"Fields of Testing"
which accompany this Certificate.

Continued accredited status depends on successful completion of on-site inspection, proficiency testing studies, and payment of applicable fees.

This Certificate is granted in accordance with provisions of Section 100825, et seq. of the Health and Safety Code.

Certificate No.: **2944**

Expiration Date: **9/30/2018**

Effective Date: **10/1/2016**

Sacramento, California
subject to forfeiture or revocation

Christine Sotelo, Chief
Environmental Laboratory Accreditation Program

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

CALIFORNIA STATE
ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM
Accredited Fields of Testing

Eurofins Calscience, Inc.

7440 Lincoln Way
Garden Grove, CA 92841-1427
Phone: (714) 895-5494

Certificate No. 2944
Expiration Date 9/30/2018

Field of Testing: 102 - Inorganic Chemistry of Drinking Water

102.015	001	Hydrogen Ion (pH)	EPA 150.1
102.020	001	Turbidity	EPA 180.1
102.026	001	Calcium	EPA 200.7
102.026	002	Magnesium	EPA 200.7
102.026	003	Potassium	EPA 200.7
102.026	004	Silica	EPA 200.7
102.026	005	Sodium	EPA 200.7
102.026	006	Hardness (calculation)	EPA 200.7
102.030	001	Bromide	EPA 300.0
102.030	003	Chloride	EPA 300.0
102.030	005	Fluoride	EPA 300.0
102.030	006	Nitrate (as N)	EPA 300.0
102.030	007	Nitrite (as N)	EPA 300.0
102.030	008	Phosphate, Ortho (as P)	EPA 300.0
102.030	009	Sulfate	EPA 300.0
102.040	003	Chlorate	EPA 300.1
102.045	001	Perchlorate	EPA 314.0
102.047	001	Perchlorate	EPA 331.0
102.060	001	Nitrate (as N) (Calculation)	EPA 353.2
102.061	001	Nitrite	EPA 353.2
102.070	001	Phosphate, Ortho	EPA 365.1
102.095	001	Turbidity	SM2130B-2001
102.100	001	Alkalinity	SM2320B-1997
102.120	001	Hardness (calculation)	SM2340B-1997
102.121	001	Hardness	SM2340C-1997
102.130	001	Conductivity	SM2510B-1997
102.140	001	Residue, Filterable TDS	SM2540C-1997
102.148	001	Calcium	SM3500-Ca B-1997
102.174	001	Chlorine, Free	SM4500-Cl F-2000
102.174	002	Chlorine, Total Residual	SM4500-Cl F-2000
102.175	001	Chlorine, Free	SM4500-Cl G-2000
102.175	002	Chlorine, Total Residual	SM4500-Cl G-2000
102.190	001	Cyanide, Total	SM4500-CN E
102.192	001	Cyanide, amenable	SM4500-CN G
102.200	001	Fluoride	SM4500-F C-1997
102.203	001	Hydrogen Ion (pH)	SM4500-H+ B-2000
102.220	001	Nitrite (as N)	SM4500-NO2- B-2000
102.240	001	Phosphate, Ortho (as P)	SM4500-P E-1999

As of 9/28/2016 , this list supersedes all previous lists for this certificate number.
Customers: Please verify the current accreditation standing with the State.

102.260	001	Total Organic Carbon TOC	SM5310B-2000
102.261	001	Dissolved Organic Carbon (DOC)	SM5310B-2000
102.264	001	Total Organic Carbon TOC	SM5310D-2000
102.265	001	Dissolved Organic Carbon (DOC)	SM5310D-2000

Field of Testing: 103 - Toxic Chemical Elements of Drinking Water

103.130	001	Aluminum	EPA 200.7
103.130	003	Barium	EPA 200.7
103.130	004	Beryllium	EPA 200.7
103.130	005	Cadmium	EPA 200.7
103.130	007	Chromium	EPA 200.7
103.130	008	Copper	EPA 200.7
103.130	009	Iron	EPA 200.7
103.130	011	Manganese	EPA 200.7
103.130	012	Nickel	EPA 200.7
103.130	015	Silver	EPA 200.7
103.130	017	Zinc	EPA 200.7
103.130	018	Boron	EPA 200.7
103.140	001	Aluminum	EPA 200.8
103.140	002	Antimony	EPA 200.8
103.140	003	Arsenic	EPA 200.8
103.140	004	Barium	EPA 200.8
103.140	005	Beryllium	EPA 200.8
103.140	006	Cadmium	EPA 200.8
103.140	007	Chromium	EPA 200.8
103.140	008	Copper	EPA 200.8
103.140	009	Lead	EPA 200.8
103.140	010	Manganese	EPA 200.8
103.140	012	Nickel	EPA 200.8
103.140	013	Selenium	EPA 200.8
103.140	014	Silver	EPA 200.8
103.140	015	Thallium	EPA 200.8
103.140	016	Zinc	EPA 200.8
103.140	017	Boron	EPA 200.8
103.140	018	Vanadium	EPA 200.8
103.160	001	Mercury	EPA 245.1
103.310	001	Chromium (VI)	EPA 218.6

Field of Testing: 104 - Volatile Organic Chemistry of Drinking Water

104.030	001	1,2-Dibromoethane	EPA 504.1
104.030	002	1,2-Dibromo-3-chloropropane	EPA 504.1
104.035	001	1,2,3-Trichloropropane	SRL 524M-TCP
104.040	000	Volatile Organic Compounds	EPA 524.2

Field of Testing: 108 - Inorganic Chemistry of Wastewater

108.020	001	Conductivity	EPA 120.1
108.030	001	Hardness	EPA 130.1
108.090	001	Residue, Volatile	EPA 160.4
108.110	001	Turbidity	EPA 180.1

108.112	001	Boron	EPA 200.7
108.112	002	Calcium	EPA 200.7
108.112	003	Hardness (calculation)	EPA 200.7
108.112	004	Magnesium	EPA 200.7
108.112	005	Potassium	EPA 200.7
108.112	006	Silica, Dissolved	EPA 200.7
108.112	007	Sodium	EPA 200.7
108.112	008	Phosphorus, Total	EPA 200.7
108.113	001	Boron	EPA 200.8
108.113	002	Calcium	EPA 200.8
108.113	003	Magnesium	EPA 200.8
108.113	004	Potassium	EPA 200.8
108.113	005	Silica, Dissolved	EPA 200.8
108.113	006	Sodium	EPA 200.8
108.120	001	Bromide	EPA 300.0
108.120	002	Chloride	EPA 300.0
108.120	003	Fluoride	EPA 300.0
108.120	008	Sulfate	EPA 300.0
108.120	012	Nitrate (as N)	EPA 300.0
108.120	013	Nitrate-Nitrite (as N)	EPA 300.0
108.120	014	Nitrite (as N)	EPA 300.0
108.120	015	Phosphate, Ortho (as P)	EPA 300.0
108.141	001	Alkalinity	EPA 310.2
108.183	001	Cyanide, Total	EPA 335.4
108.209	001	Ammonia (as N)	EPA 350.1
108.211	002	Kjeldahl Nitrogen, Total (as N)	EPA 351.2
108.260	001	Phosphate, Ortho	EPA 365.1
108.261	001	Phosphorus, Total	EPA 365.1
108.264	001	Phosphate, Ortho	EPA 365.3
108.265	001	Phosphorus, Total	EPA 365.3
108.323	001	Chemical Oxygen Demand	EPA 410.4
108.360	001	Phenols, Total	EPA 420.1
108.381	001	Oil and Grease	EPA 1664A
108.385	001	Color	SM2120B-2001
108.390	001	Turbidity	SM2130B-2001
108.400	001	Acidity	SM2310B-1997
108.410	001	Alkalinity	SM2320B-1997
108.420	001	Hardness (calculation)	SM2340B-1997
108.421	001	Hardness	SM2340C-1997
108.430	001	Conductivity	SM2510B-1997
108.439	001	Residue, Volatile	SM2540E-1997
108.440	001	Residue, Total	SM2540B-1997
108.441	001	Residue, Filterable TDS	SM2540C-1997
108.442	001	Residue, Non-filterable TSS	SM2540D-1997
108.443	001	Residue, Settleable	SM2540F-1997
108.449	001	Calcium	SM3500-Ca B-1997
108.451	001	Chloride	SM4500-Chloride C-1997

108.464	001	Chlorine, Total Residual	SM4500-Cl F-2000
108.464	002	Chlorine, Free	SM4500-Cl F-2000
108.472	001	Cyanide, Total	SM4500-CN E-1999
108.473	001	Cyanide, amenable	SM4500-CN G-1999
108.480	001	Fluoride	SM4500-F B,C-1997
108.490	001	Hydrogen Ion (pH)	SM4500-H+ B-2000
108.500	002	Ammonia (as N)	SM4500-NH3 B,C-1997
108.501	002	Kjeldahl Nitrogen, Total (as N)	SM4500-NH3 C-1997
108.502	002	Ammonia (as N)	SM4500-NH3 B,E-1997
108.503	002	Kjeldahl Nitrogen, Total (as N)	SM4500-NH3 B,D-1997
108.504	002	Ammonia (as N)	SM4500-NH3 F-1997
108.511	001	Kjeldahl Nitrogen, Total (as N)	SM4500-Norg B- 1997
108.513	001	Kjeldahl Nitrogen, Total (as N)	SM4500-Norg D-1997
108.514	001	Nitrite (as N)	SM4500-NO2- B-2000
108.528	001	Nitrate-Nitrite (as N)	SM4500-NO3- E-2000
108.528	002	Nitrite (as N)	SM4500-NO3- E-2000
108.536	001	Oxygen, dissolved	SM4500-O G-2001
108.540	001	Phosphate, Ortho (as P)	SM4500-P E-1999
108.541	001	Phosphorus, Total	SM4500-P E-1999
108.584	001	Sulfide (as S)	SM4500-S= D-2000
108.592	001	Biochemical Oxygen Demand	SM5210B-2001
108.592	002	Carbonaceous BOD	SM5210B-2001
108.595	001	Chemical Oxygen Demand	SM5220D-1997
108.596	001	Organic Carbon-Total (TOC)	SM5310B-2000
108.598	001	Organic Carbon-Total (TOC)	SM5310D-2000
108.603	001	Oil & Grease Total	SM5520B-2001
108.605	001	Surfactants	SM5540C-2000

Field of Testing: 109 - Toxic Chemical Elements of Wastewater

109.010	001	Aluminum	EPA 200.7
109.010	002	Antimony	EPA 200.7
109.010	003	Arsenic	EPA 200.7
109.010	004	Barium	EPA 200.7
109.010	005	Beryllium	EPA 200.7
109.010	006	Boron	EPA 200.7
109.010	007	Cadmium	EPA 200.7
109.010	009	Chromium	EPA 200.7
109.010	010	Cobalt	EPA 200.7
109.010	011	Copper	EPA 200.7
109.010	012	Iron	EPA 200.7
109.010	013	Lead	EPA 200.7
109.010	015	Manganese	EPA 200.7
109.010	016	Molybdenum	EPA 200.7
109.010	017	Nickel	EPA 200.7
109.010	019	Selenium	EPA 200.7
109.010	021	Silver	EPA 200.7
109.010	023	Thallium	EPA 200.7
109.010	024	Tin	EPA 200.7

109.010	025	Titanium	EPA 200.7
109.010	026	Vanadium	EPA 200.7
109.010	027	Zinc	EPA 200.7
109.020	001	Aluminum	EPA 200.8
109.020	002	Antimony	EPA 200.8
109.020	003	Arsenic	EPA 200.8
109.020	004	Barium	EPA 200.8
109.020	005	Beryllium	EPA 200.8
109.020	006	Cadmium	EPA 200.8
109.020	007	Chromium	EPA 200.8
109.020	008	Cobalt	EPA 200.8
109.020	009	Copper	EPA 200.8
109.020	010	Lead	EPA 200.8
109.020	011	Manganese	EPA 200.8
109.020	012	Molybdenum	EPA 200.8
109.020	013	Nickel	EPA 200.8
109.020	014	Selenium	EPA 200.8
109.020	015	Silver	EPA 200.8
109.020	016	Thallium	EPA 200.8
109.020	017	Vanadium	EPA 200.8
109.020	018	Zinc	EPA 200.8
109.020	020	Gold	EPA 200.8
109.020	021	Iron	EPA 200.8
109.020	022	Tin	EPA 200.8
109.020	023	Titanium	EPA 200.8
109.104	001	Chromium (VI)	EPA 218.6
109.190	001	Mercury	EPA 245.1
109.361	001	Mercury	EPA 1631E

Field of Testing: 110 - Volatile Organic Chemistry of Wastewater

110.020	000	Purgeable Aromatics	EPA 602
110.040	000	Purgeable Organic Compounds	EPA 624

Field of Testing: 111 - Semi-volatile Organic Chemistry of Wastewater

111.060	000	Polynuclear Aromatics	EPA 610
111.093	000	Chlorinated Herbicides	EPA 615
111.100	000	Base/Neutral & Acid Organics	EPA 625
111.170	000	Organochlorine Pesticides and PCBs	EPA 608

Field of Testing: 114 - Inorganic Chemistry of Hazardous Waste

114.010	001	Antimony	EPA 6010B
114.010	002	Arsenic	EPA 6010B
114.010	003	Barium	EPA 6010B
114.010	004	Beryllium	EPA 6010B
114.010	005	Cadmium	EPA 6010B
114.010	006	Chromium	EPA 6010B
114.010	007	Cobalt	EPA 6010B
114.010	008	Copper	EPA 6010B
114.010	009	Lead	EPA 6010B

114.010	010	Molybdenum	EPA 6010B	
114.010	011	Nickel	EPA 6010B	
114.010	012	Selenium	EPA 6010B	
114.010	013	Silver	EPA 6010B	
114.010	014	Thallium	EPA 6010B	
114.010	015	Vanadium	EPA 6010B	
114.010	016	Zinc	EPA 6010B	
114.020	001	Antimony	EPA 6020	
114.020	002	Arsenic	EPA 6020	
114.020	003	Barium	EPA 6020	
114.020	004	Beryllium	EPA 6020	
114.020	005	Cadmium	EPA 6020	
114.020	006	Chromium	EPA 6020	
114.020	007	Cobalt	EPA 6020	
114.020	008	Copper	EPA 6020	
114.020	009	Lead	EPA 6020	
114.020	010	Molybdenum	EPA 6020	
114.020	011	Nickel	EPA 6020	
114.020	012	Selenium	EPA 6020	
114.020	013	Silver	EPA 6020	
114.020	014	Thallium	EPA 6020	
114.020	015	Vanadium	EPA 6020	
114.020	016	Zinc	EPA 6020	
114.103	001	Chromium (VI)	EPA 7196A	
114.106	001	Chromium (VI)	EPA 7199	
114.130	001	Lead	EPA 7420	
114.140	001	Mercury	EPA 7470A	
114.141	001	Mercury	EPA 7471A	
114.222	001	Cyanide	EPA 9014	
114.230	001	Sulfides, Total	EPA 9034	
114.240	001	Corrosivity - pH Determination	EPA 9040B	
114.241	001	Corrosivity - pH Determination	EPA 9045C	
114.250	001	Fluoride	EPA 9056	

Field of Testing: 115 - Extraction Test of Hazardous Waste

115.020	001	Toxicity Characteristic Leaching Procedure (TCLP)	EPA 1311	
115.021	001	TCLP Inorganics	EPA 1311	
115.022	001	TCLP Extractables	EPA 1311	
115.023	001	TCLP Volatiles	EPA 1311	Interim
115.030	001	Waste Extraction Test (WET)	CCR Chapter11, Article 5, Appendix II	
115.040	001	Synthetic Precipitation Leaching Procedure (SPLP)	EPA 1312	

Field of Testing: 116 - Volatile Organic Chemistry of Hazardous Waste

116.020	030	Nonhalogenated Volatiles	EPA 8015B	
116.020	031	Ethanol and Methanol	EPA 8015B	
116.030	001	Gasoline-range Organics	EPA 8015B	
116.040	041	Methyl tert-butyl Ether (MTBE)	EPA 8021B	
116.040	061	Aromatic Volatiles	EPA 8021B	

116.080	000	Volatile Organic Compounds	EPA 8260B	
116.080	120	Oxygenates	EPA 8260B	
116.100	001	Total Petroleum Hydrocarbons - Gasoline	LUFT GC/MS	
116.100	010	BTEX and MTBE	LUFT GC/MS	
116.110	001	Total Petroleum Hydrocarbons - Gasoline	LUFT	
Field of Testing: 117 - Semi-volatile Organic Chemistry of Hazardous Waste				
117.010	001	Diesel-range Total Petroleum Hydrocarbons	EPA 8015B	
117.016	001	Diesel-range Total Petroleum Hydrocarbons	LUFT	
117.110	000	Extractable Organics	EPA 8270C	
117.140	000	Polynuclear Aromatic Hydrocarbons	EPA 8310	
117.170	000	Nitroaromatics and Nitramines	EPA 8330	
117.171	000	Nitroaromatics and Nitramines	EPA 8330A	
117.210	000	Organochlorine Pesticides	EPA 8081A	
117.220	000	PCBs	EPA 8082	
117.240	000	Organophosphorus Pesticides	EPA 8141A	
117.250	000	Chlorinated Herbicides	EPA 8151A	
Field of Testing: 119 - Toxicity Bioassay of Hazardous Waste				
119.010	001	Fathead Minnow (P. promelas)	Polisini & Miller (CDFG 1988)	Interim
Field of Testing: 120 - Physical Properties of Hazardous Waste				
120.010	001	Ignitability	EPA 1010	
120.022	001	Ignitability	EPA 1030	
120.040	001	Reactive Cyanide	Section 7.3 SW-846	
120.050	001	Reactive Sulfide	Section 7.3 SW-846	
120.070	001	Corrosivity - pH Determination	EPA 9040B	
120.080	001	Corrosivity - pH Determination	EPA 9045C	

NELAP

Quality Manual

QUALITY SYSTEMS MANUAL FOR ENVIRONMENTAL ANALYTICAL SERVICES

eurofins | Calscience

Version 5.7
June 2015

Prepared By

Eurofins Calscience, Inc.
7440 Lincoln Way
Garden Grove, CA 92841-1427
Telephone: 714-895-5494
Facsimile: 714-894-7501
Internet: www.calscience.com

Based On

The NELAC Institute (TNI)
National Environmental Laboratory Accreditation Program (NELAP)
Management and Technical Requirements for Laboratories Performing Environmental Analysis
TNI Standard (EL-V1-2009) Effective September 09, 2009

Larry Lem
QUALITY ASSURANCE MANAGER

Linda Scharpenberg
QUALITY ASSURANCE / TECHNICAL DIRECTOR

Virginia Huang
OPERATIONS DIRECTOR

Elizabeth Winger
LABORATORY DIRECTOR

Steven L. Lane
VICE-PRESIDENT / BUSINESS UNIT MANAGER

TABLE OF CONTENTS
QUALITY SYSTEMS MANUAL

PREFACE TO THE QUALITY SYSTEMS MANUAL

Purpose

The purpose of this document is to provide implementation guidance on the establishment and management of quality systems for Eurofins Calscience, Inc (ECI) and is based on the National Environmental Laboratory Accreditation Conference's (NELAC) Quality System requirements, the Department of Defense / Energy Environmental Laboratory Accreditation Program (DOD/DOE ELAP) and International Organization for Standardization / International Electrotechnical Commission (ISO/IEC) 17025:2005.

These three programs are built upon one another and are mutually reinforcing in their Quality Assurance programs and protocols.

Background

To be accredited and in compliance under the following three programs:

1. The National Environmental Laboratory Accreditation Program (NELAP). Accredited laboratories shall have a comprehensive quality system in place, the requirements for which are outlined in The NELAC Institute (TNI) 2009 Volume 1: Management and Technical Requirements for Laboratories Performing Environmental Analysis (EL-V1-2009). This manual was written with guidance primarily from Volume 1: Modules 2, 3, 4, 5, and 7.

   Additional information may be found at:

   - http://www.nelac-institute.org/

2. The Department of Defense Environmental Laboratory Accreditation Program (DOD/DOE ELAP) will provide a means for laboratories to demonstrate conformance to the DOD/DOE Quality Systems Manual for Environmental Laboratories (DOD/DOE QSM) as authorized by DOD Instruction 4715.15.

   The DOD/DOE QSM Revision 5.0 (July 2013) is based on the National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems standard which provides guidelines for implementing the international standard, ISO/IEC 17025.

   Additional information may be found at:

   - http://www.denix.osd.mil/edqw/Accreditation/
   - http://www.denix.osd.mil/edqw/upload/QSM-Version-5-0-FINAL.pdf

3. ISO/IEC 17025:2005 General Requirements for the Competence of Testing and Calibration Laboratories is for use by laboratories in developing their management system for quality, administrative and technical operations. Laboratory customers, regulatory authorities and accreditation bodies may also use it in confirming or recognizing the competence of laboratories.

   Additional information may be found at:

   - http://www.iso.org/iso/home.html

Project Specific Requirements

Project-specific requirements or regulations may supersede requirements contained in this manual. The laboratory bears the responsibility for meeting all **State requirements**. Nothing in this document relieves the laboratory from complying with contract requirements, or with **Federal, State, and/or local regulations**.

Results and Benefits

- **Standardization of Processes** – Because this manual provides the laboratory with a comprehensive set of requirements that meet the needs of many clients, as well as the NELAP, the laboratory may use it to create a standardized quality system. Ultimately, this standardization saves laboratory resources by establishing one set of consistent requirements for all environmental work. Primarily, the laboratory bears the responsibility for meeting all State requirements as outlined in their respective certification programs.

- **Deterrence of Improper, Unethical, or Illegal Actions** – Improper, unethical, or illegal activities committed by only a few laboratories have implications throughout the industry, with negative impacts on all laboratories. This manual establishes a minimum threshold program for all laboratories to use to deter and detect improper, unethical, or illegal actions.

- **Foundations for the Future** – A standardized approach to quality systems, shared by laboratories and The NELAC Institute, paves the way for the standardization of other processes. For example, this manual might serve as a platform for a standardized strategy for Performance Based Measurement System (PBMS) implementation.

Document Format

This ECI Quality Systems Manual (QSM) is designed to implement the TNI 2009 (EL-V1-2009) standards along with the DOD/DOE QSM 5.0 and the ISO/IEC 17025:2005 standards.

The section numbering has been changed from that of these standards as the manual is meant to be a stand-alone document. Thus the numbering in this document is not consistent with the numbering in the above-mentioned standards; however, all required elements are covered, herein.
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ACROYNM LIST

°C: Degrees Celsius
ANSI/ASQC: American National Standards Institute / American Society for Quality Control
ASTM: American Society for Testing and Materials
CAS: Chemical Abstract Service
CCV: Continuing calibration verification
CFR: Code of Federal Regulations
CLP: Contract Laboratory Program
COC: Chain of Custody
CV: Coefficient of Variation
DO: Dissolved Oxygen
DOC: Demonstration of Capability
DOD/DOE: Department of Defense / Energy
DQOs: Data Quality Objectives
EPA: Environmental Protection Agency
g/L: Grams per Liter
GC/MS: Gas Chromatography / Mass Spectrometry
ICP-MS: Inductively Coupled Plasma / Mass Spectrometer
ICV: Initial Calibration Verification
ID: Identifier
ISO/IEC: International Standards Organization / International Electrotechnical Commission
LCS: Laboratory Control Sample
LCSD: Laboratory Control Sample Duplicate
LOD: Limit of Detection
LOQ: Limit of Quantitation
LQMP: Laboratory Quality Management Plan
MDL: Method Detection Limit
ME: Marginal Exceedance
mg/kg: Milligrams per Kilogram
MS: Matrix Spike
MSD: Matrix Spike Duplicate
NELAC: National Environmental Laboratory Accreditation Conference
NELAP: National Environmental Laboratory Accreditation Program
NIST: National Institute of Standards and Technology
OSHA: Occupational Safety and Health Administration
PBMS: Performance Based Measurement System
PC: Personal Computer
PCBs: Polychlorinated Biphenyls
PT: Proficiency Testing
QA: Quality Assurance
QAD: Quality Assurance Division (EPA)
QAMS: Quality Assurance Management Section
QAPP: Quality Assurance Project Plan
QSM: Quality Systems Manual
QC: Quality Control
RL: Reporting Limit
RPD: Relative Percent Difference
RSD: Relative Standard Deviation
SD: Serial Dilutions
SOP: Standard Operating Procedure
TNI: The NELAC Institute
TSS: Total Suspended Solids
UV: Ultraviolet
VOC: Volatile Organic Compound

QUALITY SYSTEMS

Quality Systems include all quality assurance (QA) policies and quality control (QC) procedures that are delineated in a Quality Systems Manual (QSM) and followed to ensure and document the quality of the analytical data. Eurofins Calscience, Inc. (ECI), accredited under the National Environmental Laboratory Accreditation Program (NELAP), assures implementation of all QA policies and the applicable QC procedures specified in this Manual. The QA policies, which establish essential QC procedures, are applicable to all areas of ECI, regardless of size and complexity.

The intent of this document is to provide sufficient detail about quality management requirements so that all accrediting authorities evaluate laboratories consistently and uniformly.

The NELAC Institute (TNI) is committed to the use of Performance Based Measurement Systems (PBMS) in environmental testing and provides the foundation for PBMS implementation in these standards. While this standard may not currently satisfy all the anticipated needs of PBMS, NELAC will address future needs within the context of State statutory and regulatory requirements and the finalized EPA implementation plans for PBMS.

Chapter 5 is organized according to the structure of ISO/IEC 17025, 2005. Where deemed necessary specific areas within this Chapter may contain more information than specified by ISO/IEC 17025.

All items identified in this QSM shall be available for on-site inspection or data audit.

1.0 SCOPE

a) This QSM sets the general requirements that ECI must successfully demonstrate to be recognized as competent to perform specific environmental tests.

b) This QSM includes additional requirements and information for assessing competence or for determining compliance by the organization or accrediting authority that grants approval.

   If more stringent standards or requirements are included in a mandated test method or by regulation, the laboratory demonstrates that such requirements are met. If it is not clear which requirements are more stringent, the standard from the method or regulation is to be followed.

c) ECI uses this QSM in the development and implementation of its quality systems. Accreditation authorities use this NELAC based standard to assess the competence of environmental laboratories.

2.0 REFERENCES

See Appendix A.

3.0 DEFINITIONS

The relevant definitions from ISO/IEC Guide 2, ANSI/ASQC E-4, 1994, the EPA “Glossary of Quality Assurance Terms and Acronyms,” and the *International vocabulary of basic and general terms in metrology (VIM*) are applicable. The most relevant is quoted in Appendix A, Glossary, of Chapter 1 of NELAC, together with further definitions applicable for the purposes of this Standard.

4.0 ORGANIZATION AND MANAGEMENT

4.1 Legal Definition of Laboratory

ECI is legally definable as evidenced by its business license, and current California State Water Resources Control Board (SWRCB) Services Environmental Laboratory Accreditation Program (ELAP) certificate. It is organized and operates in such a way that its facilities meet the requirements of the Standard. See the graphical presentations of the Organization and QA responsibility in Figures 1 and 2, respectively.

4.2 Organization

Eurofins Calscience Inc.:

a) Has a managerial staff with the authority and resources necessary to discharge their duties;

b) Has processes to ensure that its personnel are free from any commercial, financial and other undue pressure that adversely affect the quality of their work;

c) Is organized in such a way that confidence in its independence of judgment and integrity is maintained at all times;

d) Specifies and documents the responsibility, authority, and interrelationship of all personnel who manage, perform or verify work affecting the quality of calibrations and tests;

   Such documentation includes:

   1) A clear description of the lines of responsibility in the laboratory, and is proportioned such that adequate supervision is ensured, and

   2) Job descriptions for all positions.

e) Provides supervision by persons familiar with the calibration or test methods and procedures, the objective of the calibration or test, and the assessment of the results.

   The ratio of supervisory to non-supervisory personnel ensures adequate supervision and adherence to laboratory procedures and accepted techniques.

f) Has a technical director who has overall responsibility for the technical operation of ECI.

   The technical director certifies that personnel who perform the tests for which the laboratory is accredited have the appropriate educational and/or technical background. Such certification is documented.

   The technical director meets the requirements specified in the Accreditation Process. (See NELAC Section 4.1.1.1.)

g) Has a quality assurance manager who has responsibility for the quality system and its implementation.

   The quality assurance officer has direct access to the technical director and to the highest level of management at which decisions are made regarding laboratory policy or resources.

   The quality assurance manager (and/or his/her designees):

   1) Serves as the focal point for QA/QC activities, and is responsible for the oversight and/or review of quality control data;

2) Has functions independent from laboratory operations for which she/he has quality assurance oversight;

3) Is able to evaluate data objectively and perform assessments without outside (e.g., managerial) influence;

4) Has documented training and/or experience in QA/QC procedures and is knowledgeable in the quality system, as defined under NELAC;

5) Has a general knowledge of the analytical test methods for which data review is performed;

6) Arranges for and conducts internal audits as per ECI QSM section 5.3 annually; and

7) Notifies ECI management of deficiencies in the quality system and monitors corrective action.

h) Nominates, by way of the "Alternates List," deputies in case of absence of the Technical Director and/or the Quality Assurance Director;

i) ECI makes every effort to ensure the protection of its clients' information as confidential and proprietary.

ii) ECI is sensitive to the fact that much of the analytical work performed for clientele may be subject to litigation processes. ECI, therefore, holds all information in strict confidence with laboratory release only to the client.

iii) Information released to entities other than the client is performed only upon written request from the client.

iv) Due to the investigative nature of most site assessments, analytical information may become available to regulatory agencies or other evaluating entities during site assessment of the laboratory for the specific purpose of attaining laboratory certifications, accreditations, or evaluation of laboratory qualification for future work. During these occurrences, the laboratory will make every effort to maintain the confidence of client specific information.

j) For purposes of qualifying for and maintaining accreditation, participates in a proficiency test program as outlined in Chapter 2 of NELAC. Results of ECI's performance in rounds of proficiency testing are available by request or on the web site.

5.0 QUALITY SYSTEM – ESTABLISHMENT, AUDITS, ESSENTIAL QUALITY CONTROLS, AND DATA VERIFICATION

5.1 Establishment

ECI establishes and maintains quality systems based on the required elements contained in this Manual and appropriate to the type, range and volume of environmental testing activities it undertakes.

a) The elements of this quality system are documented in this quality manual.

b) The quality documentation is available for use by all laboratory personnel.

c) The laboratory defines and documents its policies and objectives for, and its commitment to accepted laboratory practices and quality of testing services.

d) The laboratory management ensures that these policies and objectives are documented in the quality manual and are communicated to, understood and implemented by all laboratory personnel concerned.

i. All staff members are given access to a controlled copy of the Quality Systems Manual (QSM) for review at the commencement of employment. However, the individual Standard Operating Procedures are the training documents that have precedence. The QSM is provided as a general overview.

ii. A controlled copy of the quality manual is also available in each department.

e) The quality manual is maintained current under the responsibility of the quality assurance department. This manual is reviewed on an annual basis or more frequently, and revised as necessary.

5.2 Quality Systems Manual (QSM) Elements

This Quality Systems Manual (QSM) and related quality documentation state ECI's policies and operational procedures established in order to meet the requirements of this Standard.

This manual lists on the title page: a document title; the laboratory's full name and address; the name, address, and telephone number of individuals responsible for the laboratory and the effective date of the version.

This quality manual and related quality documentation also contains:

a) A quality ***policy statement***, including objectives and commitments, by top management;

i. Eurofins Calscience, Inc. (ECI) is committed to providing the highest quality environmental analytical services available. To ensure the production of scientifically sound, legally defensible data of known and proven quality, an extensive Quality Assurance program has been developed and implemented. This document, ECI's Quality Systems Manual for Environmental Analytical Services, presents an overview of the essential elements of our Quality Assurance program. ECI has modeled this systems manual after EPA guidelines as outlined in "Guidance for Quality Assurance Project Plans (EPA QA/G-5)", Office of Monitoring Systems and Quality Assurance, Office of Research and Development, U.S. EPA, EPA/240-R-02/009 December 2002. ECI's QA Program is closely monitored at the Corporate, Divisional, and Group levels, and relies on clearly defined objectives, well-documented procedures, a comprehensive quality assurance/quality control system, and management support for its effectiveness.

ii. This QA Program Systems Manual is designed to control and monitor the quality of data generated at ECI. The essential elements described herein are geared toward generating data that is in compliance with federal regulatory requirements specified under the Clean Water Act, the Safe Drinking Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation, and Liability Act, and applicable amendments, and state and DOD/DOE/DoE equivalents. Although the quality control requirements of these various programs are not completely consistent, each of the programs base data quality judgments on the following three types of information, the operational elements of each being described elsewhere in this manual.

⇨ Data which indicates the overall qualifications of the laboratory to perform environmental analyses;
⇨ Data which measures the laboratory's daily performance using a specific method; and
⇨ Data which measures the effect of a specific matrix on the performance of a method.

iii. It is important to note that the QA guidelines presented herein will always apply unless adherence to specific Quality Assurance Project Plans (QAPPs) or client and/or regulatory agency specific requirements are directed. In these cases, the elements contained within specified direction or documentation shall supersede that contained herein.

iv. This manual is a living document subject to periodic modifications to comply with regulatory changes and technological advancements. All previous versions of this document are obsolete. Users are urged to contact ECI to verify the current revision of this document.

b) The organization and management structure of the laboratory, its place in any parent organization and relevant organizational charts;

See Figure 1 Organizational Chart, and Figure 2 and 3 Responsibility Charts.

c) The relationship between management, technical operations, support services and the quality system;

d) Procedures to ensure that all records required under the NELAP are retained, as well as procedures for control and maintenance of documentation through a document control system which ensures that all standard operating procedures, manuals, or documents clearly indicate the time period during which the procedure or document was in force;

i. Ensuring a high quality work product in the environmental laboratory not only requires adherence to the quality issues discussed in the previous sections, but also requires the ability to effectively archive, restore, and protect the records that are generated.

ii. Procedures are in place to ensure that all records are retained. In addition, a documentation control system is employed to clearly indicate the time period during which a standard operating procedure, manual, or document was in force. These procedures are outlined in the laboratory standard operating procedure SOP-T002.

iii. All laboratory logbooks, instrument response printouts, completed analytical reports, chain-of-custodies, and laboratory support documentation are stored for a minimum of five years. Project specific data are stored in sequentially numbered project files and include copies of the applicable laboratory logbooks, instrument response printouts, completed analytical reports, chain-of-custodies, and any other pertinent supporting documentation.

iv. When complete, the project specific data are high speed optically scanned and transformed into digital CD media. Additional copies of these records are created at the time of scanning and are stored off-site for protection of the data. These records are stored for a minimum of five years.

v. Access to all systems is limited by use of log-in and password protection and is maintained by the system administrator.

vi. There are four forms of electronic data that are generated in the laboratory. Refer to Table 1 – Data Archiving Schedule below for a synopsis of general data archiving schedules.

vii. All electronic records are stored for a minimum of five years.

TABLE 1 – DATA ARCHIVING SCHEDULE

<u>LIMS Database</u>	
Backup frequency:	Daily
Backup media:	Hard Disk
Backup software:	MS SQL Server Backup
Backup versions kept:	Ten previous versions
Onsite copy:	Redundancy by using mirrored hard drive
Offsite copy:	One (Replicate to Lampson Facility)
<u>Instrument Data</u>	

Backup frequency:	Daily
Backup media:	Hard Disk
Backup software:	NT Backup
Backup versions kept:	All versions
Offsite copy:	One (Replicate to Lampson Facility)

e) Job Descriptions, Roles and Responsibilities

In order for the Quality Assurance Program to function properly, all members of the staff must clearly understand and meet their individual responsibilities as they relate to their job function and the quality program as a whole.

The responsibility for quality lies with every employee at ECI. As such, all employees have access to the Quality Assurance Manual and are responsible for knowing the content of this manual and upholding the standards therein. Each employee is expected to conduct themselves in accordance with the procedures in this manual and the laboratory's SOPs.

The following descriptions define the primary roles and their relationship to the Quality Assurance Program. Members of the key staff include the following:

- Management (e.g., President, Vice-President, Business Unit Manager, Laboratory Director);
- Technical managers (e.g., Technical Director, Section Supervisors);
- Quality managers;
- Support systems and administrative managers (e.g., IT manager, Facilities manager, project managers); and
- Other staff

In these positions, members of the key staff are responsible for assuring compliance with the National Environmental Laboratory Accreditation Program (NELAP), California Environmental Laboratory Accreditation Program (ELAP), Department of Defense / Energy (DOD/DOE) ELAP, State and Federal Agencies, and ISO 17025:2005 Standard requirements. In these roles, key personnel may set or enforce quality policies, monitor compliance, initiate corrective actions, interface with laboratory, client, and regulatory personnel, and provide general program oversight.

Business Unit Manager:

ECI's Business Unit Manager represents ECI to the Eurofins US and Global Corporate entities.

- ⇨ Ensures that ECI's financial and production performance meets assigned metrics.
- ⇨ Determines need for capital and employee resources and allocates as appropriate.
- ⇨ Serves as the legal representative for ECI.
- ⇨ Responsible for yearly budget and overruns.
- ⇨ Point person for major new initiatives

Laboratory Director:

ECI's Laboratory Director, through its Business Unit Manager, is the final authority on all issues dealing with data quality and has the authority to require that procedures be amended or discontinued, or analytical results voided or repeated. He or she also has the authority to suspend or terminate employees on the grounds of non-compliance with QA/QC procedures. In addition, the Laboratory Director:

- ⇨ Ensures that ECI remains current with all regulations which affect operations and disseminate all such changes in regulatory requirements to the QA Director, Technical Director, QA Manager, and Group Leaders;
- ⇨ Provides one or more Technical Directors for the appropriate fields of testing. The name(s) of the Technical Director are included in the national database. (The Laboratory Director may also act in the Technical Director capacity.) If the Technical Director is absent for a period of time exceeding 15 consecutive calendar days, the Laboratory Director will designate another full time staff member meeting the qualifications of the Technical Director to temporarily perform this function. If the absence exceeds 35 consecutive calendar days, the primary accrediting authority will be notified in writing;
- ⇨ Ensures that all analysts and supervisors have the appropriate education and training to properly carry out the duties assigned to them and ensures that this training has been documented;
- ⇨ Ensures that personnel are free from any commercial, financial and other undue pressures which might adversely affect the quality of their work;
- ⇨ Oversees the development and implementation of the QA Program which assures that all data generated will be scientifically sound, legally defensible, and of known quality;
- ⇨ In conjunction with the QA Manager, conducts annual reviews of the QA Program;
- ⇨ Oversees the implementation of new and revised QA procedures to improve data quality;
- ⇨ Ensures that appropriate corrective actions are taken to address analyses Identified as requiring such actions by internal and external performance or procedural audits. Procedures that do not meet the standards set forth in the QAM or laboratory SOPs may be temporarily suspended by the Laboratory Director;
- ⇨ Reviews and approves all SOPs prior to their implementation and ensures all approved SOPs are implemented and adhered to;
- ⇨ Oversees all laboratory accreditation efforts

Operations Director:

The Operations Director manages and directs the analytical production sections of the laboratory. He or she reports directly to the Laboratory Director and assists in determining the most efficient instrument utilization. More specifically, he/she:

- ⇨ Evaluate the level of internal/external non-conformances for all departments;
- ⇨ Continuously evaluate production capacity and improves capacity utilization;
- ⇨ Continuously evaluate turnaround time and addresses any problems that may hinder meeting the required and committed turnaround time from the various departments;
- ⇨ Develop and improve the training of all analysts in cooperation with the Laboratory Director, QA Director, QA Manager and Group Leaders, and in compliance with regulatory requirements;
- ⇨ Ensure that scheduled instrument maintenance is completed;
- ⇨ Are responsible for efficient utilization of supplies;
- ⇨ Constantly monitor and modify the processing of samples through the departments; and
- ⇨ Maintain sufficient personnel, equipment and supplies to achieve production goals.

Technical Director:

The Technical Director reports to the Business Unit Manager and is responsible for all laboratory, client, and project technical issues. More specifically, he/she:

- ⇨ For major projects and/or clients, act as a technical resource for the client and the laboratory in matters of method selection or QC criteria.
- ⇨ Company-wide, maintains all training-related documentation in a single secure location. Develops training guides and other training documentation as needed;

- ⇨ Interface directly with Project Management staff in response to questions pre-release or from the client post-release. Determine causation and interface with QA staff to prevent recurrences;
- ⇨ Interface directly with clients, or other client representatives in matters related to technical data quality requests.
- ⇨ Attend client, Business Development, or industry meetings with or without management when a 'technical representative' is required or would be beneficial to ECI.
- ⇨ Provide support to Business Development through the review of DOD/DOE-related SAPs, QAPPs, and work plans. Provide comment and alternative solutions if unable to meet specific requirements. Populate DOD/DOE UFP QAPP tables for client SAPs/QAPPs when needed;
- ⇨ Support QA and Operations with SOP revisions, where needed;
- ⇨ Perform full QA reviews and/or data validation where required;
- ⇨ Provide technical solutions to QA with regard to laboratory procedures, data quality issues, possible solutions, and appropriate corrective actions;
- ⇨ Provide technical opinions and support to Operations with regard to current procedures or new method development;
- ⇨ Interface with QA staff as necessary to ensure continuous improvement in all areas of ECI's operations.
- ⇨ Provide LIMS input; and
- ⇨ As may be necessary, act as Program Director for DOD/DOE or other high profile projects.

Quality Assurance Director:

The Quality Assurance (QA) Director has full authority through the Business Unit Manager in all matters relating to quality assurance and quality control systems. The QA Director can make recommendations to the Business Unit Manager and/or Laboratory Director regarding the suspension analytical activities or the suspension or termination of employees on the grounds of non-compliance with QA/QC systems or procedures. An alternate QA Director is always assigned. In the absence of the primary designate, the alternate will act in the QA Director's capacity with the full authority of the position as allowed by ECI governing documents. In addition, the QA Director performs the following:

- ⇨ Oversight and monitoring of and compliance with ECI's QA program;
- ⇨ Ensuring continuous improvement in all aspects of ECI's QA program such as:
  - o accreditations/certifications;
  - o analytical method management;
  - o internal and external audits;
  - o documentation;
  - o training;
  - o proficiency evaluation studies;
- ⇨ Ensuring ECI's QA program remains up-to-date consistent with current regulatory requirements and ECI's QA policies;
- ⇨ Supervision and direction of all QA staff; and
- ⇨ Serving as a technical resource for analytical chemistry or QA matters;
- ⇨ Provide support and oversight to QA staff with regard to external audit responses. Provide input on, and define appropriate corrective actions for the laboratory. Document corrective action responses, and monitor the required audit response time frames, as needed.
- ⇨ Oversees in-house training on quality assurance and control.

Quality Assurance Manager:

The Quality Assurance (QA) Manager has full authority through the Quality Assurance Director in matters dealing within the laboratory. The QA Manager can make recommendations to the Quality Assurance Director and/or Laboratory Director regarding the suspension or termination of employees on the grounds of

non-compliance with QA/QC procedures. An alternate QA Manager is always assigned. In the absence of the primary designate, the alternate will act in the QA Manager's capacity with the full authority of the position as allowed by ECI governing documents. In addition, the QA Manager performs the following:

- ⇨ Maintains and updates the QAM on an annual basis;
- ⇨ Implements ECI's QA Program;
- ⇨ Monitors the QA Program within the laboratory to ensure complete compliance with its objectives, QC procedures, holding times, and compliance with client or project specific data quality objectives;
- ⇨ Distributes performance evaluation (PE) samples on a routine basis to ensure the production of data that meets the objectives of its QA Program;
- ⇨ Maintains all SOPs used at ECI;
- ⇨ Maintains records and archives of all PE results, audit comments, and customer inquiries concerning the QA program;
- ⇨ Performs statistical analyses of QC data and establish controls that accurately reflect the performance of the laboratory;
- ⇨ Conducts periodic performance and system audits to ensure compliance with the elements of ECI's QA Program;
- ⇨ Prescribes and monitors corrective action;
- ⇨ Serves as in-house client representative on all project inquiries involving data quality issues;
- ⇨ Coordinates data review process to ensure that thorough reviews are conducted on all project files;
- ⇨ Develops revisions to existing SOPs;
- ⇨ Reports the status of in-house QA/QC to the Laboratory Director;
- ⇨ Maintains records and archives of all QA/QC data including but not limited to method detection limit (MDL) studies, accuracy and precision control charts, and completed log books; and
- ⇨ Conducts and/or otherwise ensures that an adequate level of QA/QC training is conducted within the laboratory.

Quality Assurance Assistant:

The QA Assistant reports to the QA Manager and performs the following functions:

- ⇨ Assists the QA Manager and lab staff with internal audits, corrective action review, test method assessments and overall implementation of the QA program;
- ⇨ Generates and reviews, in conjunction with the QA Manager, Control Charts and Method Detection Limit (MDL) studies;
- ⇨ Reviews and revises SOPs as needed;
- ⇨ Distributes new SOPs to all applicable lab areas.
- ⇨ Writes and promulgates QA Directives.

Director of Business Development:

The Director of Business Development reports to the Laboratory Director and serves as the interface between the laboratory's technical departments and the laboratory's clients. The staff consists of the Project Management team, Business Development team and satellite office Operations Manager. With the overall goal of total client satisfaction, the functions of this position are outlined below:

- ⇨ Technical training and growth of the Project Management team;
- ⇨ Business liaison for the Project Management team;
- ⇨ Human resource management of the Project Management team;
- ⇨ Responsible for the review and negotiation of client contracts and terms and conditions;

- ⇨ Responsible for establishing standard fee schedules for the laboratory;
- ⇨ Responsible for preparation of proposals and quotes for clients and client prospects;
- ⇨ Accountable for response to client inquiries concerning sample status;
- ⇨ Responsible for assistance to clients regarding the resolution of problems concerning Chains-of-Custody;
- ⇨ Ensuring that client specifications, when known, are met by communicating project and quality assurance requirements to the laboratory;
- ⇨ Notifying the department managers of incoming projects and sample delivery schedules;
- ⇨ Accountable to clients for communicating sample progress in daily status meeting with agreed-upon due dates;
- ⇨ Responsible for discussing with client any project-related problems, resolving service issues, and coordinating technical details with the laboratory staff;
- ⇨ Responsible for staff familiarization with specific quotes, sample log-in review, and final report completeness; and
- ⇨ Ensure that all non-conformance conditions are reported to the QA Manager, Operations Manager, and/or Laboratory Director via the Corrective Action process.

Technical Managers (at ECI known as Group Leaders):

The Group Leaders report directly to the Operations Director. They have the authority to accept or reject data based on pre-defined QC criteria. In addition, with the approval of the QA Manager, the Group Leaders may accept data that falls outside of normal QC limits if, in his or her professional judgment, there are technical justifications for the acceptance of such data. The circumstances must be well documented and any need for corrective action identified must be defined and initiated. The authority of the Group Leaders in QC related matters results directly from the QA Manager. The Group Leaders also

- ⇨ Coordinating, writing, and reviewing test methods and SOPs, with regard to quality, integrity, regulatory requirements and efficient production techniques;
- ⇨ Monitoring the validity of the analyses performed and data generated in the laboratory. This activity begins with reviewing and supporting all new business contracts, insuring data quality, analyzing internal and external non-conformances to identify root cause issues and implementing the resulting corrective and preventive actions, facilitating the data review process and providing technical and troubleshooting expertise on routine and unusual or complex problems;
- ⇨ Providing training and development programs to applicable laboratory staff as new hires and, subsequently, on a scheduled basis; and
- ⇨ Coordinates audit responses with supervisors and QA Manager.
- ⇨ Actively support the implementation of ECI's QA Program;
- ⇨ Ensure that their employees are in full compliance with ECI's QA Program;
- ⇨ Maintain accurate SOPs (by reviewing and implementing updates) and enforce routine compliance with SOPs;
- ⇨ Conduct technical training of new staff and when modifications are made to existing procedures;
- ⇨ Maintain a work environment which emphasizes the importance of data quality;
- ⇨ Ensure all logbooks are current, reviewed and properly labeled or archived;
- ⇨ Ensure that all non-conformance conditions are reported to the QA Manager, Operations Manager, and/or Laboratory Director via Corrective Action reports;
- ⇨ Provide guidance to analysts in resolving problems encountered daily during sample prep/analysis in conjunction with the Technical Director, Operations Manager, and/or QA Manager. Each is responsible for 100% of the data review and documentation, nonconformance issues, and the timely and accurate completion of performance evaluation samples and MDLs, for his/her department;.

- ⇨ Encourage the development of analysts to become cross-trained in various methods and/or operate multiple instruments efficiently while performing maintenance and using appropriate documentation techniques;.
- ⇨ Ensure that preventive maintenance is performed on instrumentation as detailed in the QA Manual or SOPs. He or she is responsible for developing and implementing a system for preventive maintenance, troubleshooting, and repairing or arranging for repair of instruments;
- ⇨ Provide written responses to external and internal audit issues; and
- ⇨ Provide support to all levels of ECI Management.

Technical Managers (Sample Control Group Leader):

The Sample Control Group Leader reports to the Operations Manager. The responsibilities are outlined below:

- ⇨ Direct the receipt, handling, labeling and proper storage of samples in compliance with laboratory procedures and policies;
- ⇨ Oversee the training of Sample Control Technicians regarding the above items;
- ⇨ Direct the logging of incoming samples into the LIMS and ensure the verification of data entry from login;
- ⇨ Oversee all sample courier operations;
- ⇨ Acts as a liaison between Project Managers and Analytical departments in respect to handling rush orders and resolving inconsistencies and problems with chain-of-custody forms, and routing of subcontracted analyses; and
- ⇨ Oversees the handling of samples in accordance with the Waste Disposal SOP, the Hazardous Waste Contingency Plan in the Chemical Hygiene/Safety Manual, and the U. S. Department of Agriculture requirements.

Laboratory Analysts

Laboratory analysts are responsible for conducting analysis and performing all tasks assigned to them by the group leader or supervisor. The responsibilities of the analysts are listed below:

- ⇨ Perform analyses by adhering to analytical and quality control protocols prescribed by current SOPs, this QA Manual, the Data Integrity Policy, and project-specific QA plans honestly, accurately, timely, safely, and in the most cost-effective manner.
- ⇨ Document standard and sample preparation, instrument calibration and maintenance, data calculations, sample matrix effects, and any observed non-conformance on work sheets, bench sheets, preparation logbook, and/or a Non-Conformance report;
- ⇨ Report all non-conformance situations, instrument problems, matrix problems and QC failures, which might affect the reliability of the data, to the Group Leader and/or the QA Manager;
- ⇨ Perform 100% review of the data generated prior to entering and submitting for secondary level review; and
- ⇨ Work cohesively as a team in their department to achieve the goals of accurate results, optimum turnaround time, cost effectiveness, cleanliness, complete documentation, and personal knowledge of environmental analysis.

Laboratory Technicians:

- ⇨ Prepare samples for analysis by weighing, extracting or digesting, filtering, or concentrating samples; and

- ⇨ Prepare method specific QC Samples with each preparation batch. All personnel must adhere to all QC procedures specified in the analytical method and in accordance to procedures or policies and are responsible for the full documentation of these procedures.

Project Managers:

The Project Manager normally reports to the Senior Project Manager and/or Business Development Director. Typical responsibilities include:

- ⇨ Serving as the laboratories' primary point of contact for assigned clients;
- ⇨ Working with laboratory chemists to resolve questions on data;
- ⇨ Scheduling of courier deliveries and pick-ups;
- ⇨ Tracking the progress of all laboratory production efforts;
- ⇨ Advising clients of any scheduling conflicts, possible delays, or other problems which may arise;
- ⇨ Resolving any questions or issues that clients may have with regard to our services, especially our reports;
- ⇨ Preparation of bottle kits for use by clients in their sampling efforts (as necessary);
- ⇨ Reviewing of reports/EDDs (Electronic Data Deliverables) as necessary prior to release;
- ⇨ Invoice preparation and review prior to release to client;
- ⇨ Serving as back-up contact person for other Project Managers in the event of his/her absence;
- ⇨ Coordination of all subcontracting efforts for projects assigned;
- ⇨ Preparation and implementation of program QAPPs (Quality Assurance Project Plans), if needed;
- ⇨ Preparation of project Case Narratives, as needed; and
- ⇨ Assembly of full data packages in accordance with company or client protocol, as needed.

Project Management Assistant:

The Project Management Assistant normally receives direction from the Project Manager(s) for which he/she is assigned. Typical responsibilities include:

- ⇨ Working with laboratory chemists to resolve questions on data;
- ⇨ Scheduling of courier deliveries and pick-ups;
- ⇨ Tracking the progress of all laboratory production efforts;
- ⇨ Advising clients of any scheduling conflicts, possible delays, or other problems which may arise;
- ⇨ Resolving any questions or issues that clients may have with regard to our services, especially our reports;
- ⇨ Preparation of bottle kits for use by clients in their sampling efforts;
- ⇨ Reviewing of reports/EDDs (Electronic Data Deliverables) prior to release;
- ⇨ Invoice preparation and review prior to release to client;
- ⇨ Serving as back-up contact person for the project managers in the event of his/her absence;
- ⇨ Coordination of all subcontracting efforts for projects assigned; and
- ⇨ Preparation and implementation of program QAPPs (Quality Assurance Project Plans), if needed.
- ⇨ As part of the administrative staff, this person may also be required to answer phones, do occasional filing, mailing, etc.

Health, Safety, and Respiration Protection Manager:

The Health and Safety Manager reports to the Laboratory Director and ensures that systems are maintained for the safe operation of the laboratory. The EHS Manager is responsible for:

- ⇨ Conducting ongoing, necessary safety training and conducting new employee safety orientations;
- ⇨ Assisting in developing and maintaining the Chemical Hygiene/Safety Manual;
- ⇨ Oversees the inspection and maintenance of general safety equipment – fire extinguishers, safety showers, eyewash fountains, etc. and ensure prompt repairs as needed; and
- ⇨ Completes accident reports, follows up on root causes and defines corrective actions.

Hazardous Waste Coordinator:

The Hazardous Waste Coordinator reports directly to the Environmental Health & Safety Manager. The duties of the HWC consist of:

- ⇨ Staying current with the hazardous waste regulations and continuing training on hazardous waste issues;
- ⇨ Contacting the hazardous waste subcontractors for review of procedures and opportunities for minimization of waste;
- ⇨ Supervise the recording of the transfer of samples from refrigerated conditions to ambient conditions [in the sample disposal log sheets (SDLS)];
- ⇨ Check the records in SDLS against the logbook (LIMS) records;
- ⇨ Coordinate the collection of waste throughout the laboratory that will be disposed of through “Lab Packs”;
- ⇨ Coordinate and supervise Hazardous Waste Technician(s);
- ⇨ Dispose of solid waste to an assigned Tote;
- ⇨ Supervise the recording and disposal of acid and soil with methylene chloride extracts into appropriate drums;.
- ⇨ Prepare and discharge treated wastewater to the sewer system;
- ⇨ Maintain Uniform Hazardous Waste Manifest files;
- ⇨ Prepare weekly sample disposal schedules;
- ⇨ Coordinate and schedule waste pick-up;
- ⇨ Check all waste containers for appropriate labels; and
- ⇨ Maintain safe housekeeping and practices.

Education and Experience

ECI makes every effort to hire analytical staff that posses a college degree (AA, BA, BS) in an applied science with some chemistry in the curriculum. Exceptions are made based upon experience and an individual’s ability to learn as there are many in the industry that are more than competent, experts perhaps, who have not earned a college degree.

Selection of qualified individuals for employment begins with documentation of minimum education, training, and experience prerequisites needed to perform the prescribed task. Experience and specialized training may be accepted in lieu of a college degree (basic lab skills such as using a balance, aseptic or quantitation techniques, etc. are also considered).

Included in Section 5.2 (e) of this Quality Assurance Manual are the basic job titles and personnel responsibilities for anyone who manages, performs or verifies work affecting the quality of the laboratory’s environmental sample testing. Minimum education and training requirements are summarized in the following table:

When an analyst does not meet these minimum requirements, they can perform a task under the direct supervision of a qualified analyst, peer reviewer or Group Leader, and are considered an analyst in training. The person supervising an analyst in training is directly accountable for the quality of the analytical data and must review and approve data and associated corrective actions.

Job Type	Education	Experience
Extractions, Digestions, some electrode methods (pH, DO, Redox, etc.), Titrimetric and Gravimetric Analyses,	H.S. Diploma or GED	On the job training
GFAA, CVAA, FLAA, Single component or short list Chromatography (e.g., Fuels, BTEX-GC, IC	A college degree in an applied science or 2 years of college with at least 1 year of college chemistry, or	2 years prior analytical experience is required
ICP, ICPMS, Long List or complex chromatography (e.g., Pest, PCB, Herb, HPLC, etc.), GCMS	A college degree in an applied science or 2 years of college chemistry, or	5 years of prior analytical experience is required
Spectra Interpretation	A college degree in an applied science or 2 years of college Chemistry, and	2 years relevant experience, or 5 years of prior analytical experience is required
Group Leaders – Advanced Instrumentation	Bachelors Degree in an applied science with 16 semester hours in chemistry. An advanced (MS, PhD.) degree may substitute for one year of experience, and	2 years experience in the analytical technique for environmental analysis of representative analytes for which they will oversee
Group Leaders – Wet Chemistry (Basic Skills)	Associates degree in an applied science or 2 years of college with 16 semester hours in Chemistry, and	2 years relevant experience

f) Identification of the laboratory's approved signatories; at a minimum, the title page of the quality manual has the signed and dated concurrence (with appropriate titles) of all responsible parties including the QA Manager, Operations, QA, Technical, Laboratory and Operations Directors.

g) The laboratory's procedures for achieving traceability of measurements;

h) A list of all test methods under which the laboratory performs its accredited testing may be found in the Index of Standard Operating Procedures, a separate document.

i) Mechanisms for ensuring that the laboratory reviews all new work to ensure that it has the appropriate facilities and resources before commencing such work;

j) Reference to the calibration and/or verification test procedures used;

Calibration procedures and verification of acceptability for each set of required calibrations are defined in Section 13 (Calibration) and Section 12 (Quality Control) of each standard operating procedure.

k) Procedures for handling samples received;

The generation of quality analytical data begins with the collection of the sample and, therefore, the integrity of the sample collection process is of importance to ECI. Samples must be collected in such a way that foreign material is not introduced into the samples and that analytes of interest do not escape from the samples or degrade prior to their analysis. To ensure sample integrity and representativeness, the following items must be considered:

- ⇨ Samples must be collected in appropriate containers. In general, glass containers are used for organic analytes and polyethylene for inorganic/metal analytes;
- ⇨ Only new sample containers which are certified and documented clean in accordance with U.S. EPA OSWER Directive No. 9240.0-0.05 specifications shall be provided by ECI for sample collection;
- ⇨ Certain extremely hazardous samples or samples that have the potential to become extremely hazardous will not be accepted. These include (but are not limited to)

    1. Radioactive samples that significantly exceed background levels
    2. Biohazardous samples (medical wastes, body fluids, etc.)
    3. Explosive samples in pure form (Semtex, Flash or gunpowder, ammunition, flares, etc.)
    4. Neurological or other toxic agents (Sarin, Anthrax, Ricin, etc.)

ECI's chain-of-custody document is used to forward samples from the client to the laboratory. As the basic elements of most all chain-of-custody (COC) documents are similar, clientele may choose to use their own chain-of-custody document to forward samples to ECI.

Any discrepancies in the COC must be documented on the Sample Receipt Form and resolved prior to analysis of samples. Further guidance may be found in SOP T100 “Sample Receipt and Log-In Procedures”.

Upon receipt by ECI, samples proceed through an orderly processing sequence designed to ensure continuous integrity of both the sample and its documentation from sample receipt through its analysis and beyond.

All coolers that are received by the Sample Control Group undergo a preliminary examination in accordance of the Sample Receipt Form. Specifically, each sample is carefully examined for label identification, proper container (type and volume), chemical preservation when applicable, container condition, and chain-of-custody documentation consistency with sample labels. Discrepancies are noted on both the Sample Receipt Form and the Sample Anomaly Form and, if possible, discussed with the client prior to his or her departure. If this is not possible, the discrepancies are communicated to the client for resolution prior to the completion of the log-in process. The temperature of the cooler is measured and, with other observations, is recorded.

During the log-in process each sample is assigned a unique laboratory identification number through a computerized Laboratory Information Management System (LIMS), which stores all essential project information. ECI maintains multiple security levels of access into LIMS to prevent unauthorized tampering/release of sample and project information.

Once all analyses for a sample have been completed and the sample container is returned to Sample Control, it shall remain in refrigerated storage for a period not less than 14 days following sample receipt unless the client requests return/forwarding of the sample. Following the 14-day refrigerated storage period, the samples are placed into ambient storage for another period not less than 14 days after which the samples are bulked into drums for later disposal.

Extended storage may be requested at prevailing per sample rates.

l) Reference to the major equipment and reference measurement standards used as well as the facilities and services used by the laboratory in conducting tests;

A list of major equipment is kept up-to-date on the List of Major Assets, reference Appendix G. This, as well as a list of reference measurement standards and their certificates of calibration, is maintained by the QA Manager or the respective departments. In general, all calibrations and references should be traceable to NIST

m) Reference to procedures for calibration, verification and maintenance of equipment; Laboratory SOPs (T043 and T066) are available to staff for calibration, verification and maintenance of equipment. In general,

n) Reference to verification practices which may include inter-laboratory comparisons, proficiency testing programs, use of reference materials and internal quality control schemes;

Instrument calibration is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity such that required reporting limits can be met. Each instrument is calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method. The manufacturer's guidelines, the analytical method, and/or the requirements of special contracts determine the frequency of calibration and the concentration of calibration standards, whichever is most applicable. The following are very general guidelines and are not meant to be all-inclusive. Detailed calibration procedures are specified in the SOP for each method performed.

Gas Chromatography/Mass Spectroscopy (GC/MS): Each day prior to analysis of samples, all GC/MS instruments are tuned with 4-bromofluorobenzene (BFB) for VOCs and decafluorotriphenylphosphine (DFTPP) for SVOCs in accordance with the tuning criteria specified in the applicable methods. Samples are not analyzed until the method-specific tuning requirements have been met.

After the tuning criteria are met, the instrument is then calibrated for all target analytes and an initial multipoint calibration curve established. The calibration curve is then validated by the analysis of a second source standard, referred to as the initial calibration verification (ICV). Alternatively, the previous calibration curve may be used if validated by a continuing calibration verification (CCV) standard. All target analytes are represented in the calibration and certain key target analytes referred to as system performance calibration compounds (SPCCs) and calibration check compounds (CCCs) are used for curve acceptance determination. For the initial calibration to be deemed acceptable, the SPCCs and CCCs must meet established acceptance criteria and must be re-evaluated and meet the acceptance criteria, at a minimum, every twelve (12) hours thereafter.

Non-GC/MS Chromatography: The field of chromatography involves a variety of instrumentation and detectors. While calibration standards and control criteria vary depending upon the type of system and analytical methodology required for a specific analysis, the general principles of calibration apply uniformly. Each chromatographic system is calibrated prior to sample analysis. An initial multipoint calibration curve is generated using all target analytes. All target analytes must meet the acceptance criteria for the calibration to be deemed acceptable. The calibration curve is then validated by the analysis of a second source standard, referred to as the initial calibration verification (ICV). The continued validity of the initial multipoint calibration is verified every 12 hours using continuing calibration verification (CCV) standard containing all target analytes. If the CCV fails to meet the acceptance criteria, the system is re-calibrated and all samples analyzed since the last acceptable CCV must be re-analyzed.

Inductively Coupled Plasma Emission Spectroscopy: Initial calibration consists of a calibration blank (CB) plus one calibration standard. The calibration is verified by the re-analysis of the standard and initial calibration verification (ICV) standard. If the standard and the ICV fail to meet the acceptance criteria, the initial calibration is considered invalid and is re-performed.

Continuing calibration verification (CCV) consists of a mid-concentration standard plus a calibration blank (CB) analyzed every 10 samples and at the end of the sequence. If the CCV and/or CB fail to meet the acceptance criteria, the instrument must be re-calibrated and all samples analyzed since the previous acceptable CCV and/or CB must be re-analyzed.

ICP/MS Spectroscopy: Each day prior to the analysis of samples, all ICP/MS instruments undergo mass calibration and resolution checks prior to initial calibration. Initial calibration consists of a calibration blank (CB) and at least one calibration standard. The calibration is verified by the re-analysis of the standard and initial calibration verification (ICV) standards. If the standard and the ICV fail to meet the acceptance criteria, the initial calibration is considered invalid and is re-performed.

Continuing calibration verification (CCV) consists of a mid-concentration standard plus a calibration blank (CB) analyzed every 10 samples and at the end of the sequence. If the CCV and/or CB fail to meet the acceptance criteria, the instrument must be re-calibrated and all samples analyzed since the previous acceptable CCV and/or CB must be re-analyzed.

Cold Vapor Atomic Absorption Spectroscopy: Initial calibration consists of a calibration blank plus a series of at least 5 standards. The calibration curve is then validated by the analysis of a second source standard, referred to as the initial calibration verification (ICV). Continuing calibration verification (CCV) consists of midpoint calibration standard plus a continuing calibration blank (CCB) analyzed every 10 samples and at the end of the sequence. If the CCV and/or CCB fail to meet the acceptance criteria, the instrument must be re-calibrated and all samples analyzed since the previous acceptable CCV and/or CCB must be re-analyzed. If the calibration blanks contain target analyte concentrations exceeding the acceptance limits, the cause must be determined and corrected.

Flame and Graphite Furnace Atomic Absorption Spectroscopy: Initial calibration consists of a calibration blank plus a low, medium, and high calibration standard. Continuing calibration verification (CCV) consists of midpoint calibration standard plus a continuing calibration blank (CCB) analyzed every 10 samples and at the end of the sequence. If the CCV and/or CCB fail to meet the acceptance criteria, the instrument must be re-calibrated and all samples analyzed since the previous acceptable CCV and/or CCB must be re-analyzed. If the calibration blanks contain target analyte concentrations exceeding the acceptance limits, the cause must be determined and corrected.

General Inorganic Analyses: General inorganic (non-metal) analyses involve a variety of instrumental and wet chemistry techniques. While calibration procedures vary depending on the type of instrumentation and methodology, the general principles of calibration apply universally. Each system or method is initially calibrated using standards prior to analyses being conducted with continual verification that the calibration remains acceptable throughout analytical processing. If continual calibration verification fails to meet the acceptance criteria, the instrument must be re-calibrated and all samples analyzed since the previous acceptable CCV must be re-analyzed.

o) Procedures to be followed for feedback and corrective action whenever testing discrepancies are detected, or departures from documented policies and procedures occur;

These procedures may be found in SOP-T015 (Correction/Prevention of Errors in Test Records) and SOP-T022 (Corrective/Preventive Actions).

p) The laboratory management arrangements for permitting exceptions and departures from documented policies and procedures or from standard specifications;

ECI's SOPs are in substantial conformity with their corresponding published method references. Departure from approved SOPs shall be approved if necessary or appropriate due to the nature or composition of the sample or otherwise based on the reasonable judgment of ECI's Laboratory Director, Technical Director, or QA Manager.

Departures shall be made on a case-by-case basis consistent with recognized standards of the industry. In no case shall departures be approved without written communication between EC Iand the affected client.

q) Procedures for dealing with complaints;

Procedures for dealing with complaints may be found in SOP-T018, Handling of Inquiries and Complaints.

r) Procedures for protecting confidentiality (including national security concerns) and proprietary rights;

ECI is sensitive to the fact that much of the analytical work performed for clientele may be subject to litigatory processes. ECI, therefore, holds all information in strict confidence with laboratory release only to the client or designee. Information released to entities other than the client is performed only upon written, facsimile or e-mail request from the client.

Due to the investigative nature of most site assessments, analytical information may become available to regulatory agencies or other evaluating entities during site assessment of the laboratory for the specific purpose of attaining laboratory certifications, accreditations, or evaluation of laboratory qualification for future work. During these occurrences, the laboratory will make its best effort to maintain the confidence of client specific information.

s) Procedures for audits;

ECI participates in a wide variety of system and performance audits conducted by numerous federal and state agencies, as well as through its major clientele. These audits are conducted to verify that analytical data produced conforms to industry standards on a routine basis.

A System Audit is a qualitative evaluation of the measurement systems utilized at ECI, specifically, that ECI has, in place, the necessary facilities, staff, procedures, equipment, and instrumentation to generate acceptable data. This type of audit typically involves an on-site inspection of the laboratory facility, operations, and interview of personnel by the auditing agency.

A Performance Audit verifies the ability of ECI to correctly identify and quantitate compounds in blind check samples. This type of audit normally is conducted by the auditing agency through laboratory participation in round robin Performance Evaluation (PE) programs. Examples of current PE program involvement include those offered by commercial suppliers like ERA (WS/WP/SOIL and DMR-QA), or other inter-laboratory studies not required for certification but done to ensure laboratory performance, as well as programs administered by major industry.

Outliers in required PE samples will be investigated and corrective actions documented using the Corrective/Preventive Action Record.

Should the result of any audit detect a significant error, which has been identified to adversely affect released data, the situation shall be thoroughly investigated. Corrective measures shall be enacted to include system re-evaluation, the determined affect on released data and client notification, as necessary. These measures shall be documented using the Corrective/Preventive Action Record.

t) Processes/procedures for establishing that personnel are adequately experienced in the duties they are expected to carry out and are receiving any needed training;

Quality control begins prior to sample(s) receipt at the laboratory. The selection of well qualified personnel, based upon education and/or experience is the first step in successful laboratory management. A thorough screening of job applicants and selection of the best candidate to fulfill a well-defined need is as important an aspect of a successful QA/QC program as a careful review of analytical data.

Employee training and approval procedures used at ECI are specified in SOP-T010, "Employee Training", and includes but is not limited to the following:

- ⇨ A thorough understanding of the applicable regulatory method and ECISOP;
- ⇨ A review of ECI's QA Program Manual and thorough understanding of the specifics contained therein that are directly related to the analysis to be performed;
- ⇨ Instruction by the applicable Group Leader on all aspects of the analytical procedure;
- ⇨ Performance of analyses under supervision of experienced laboratory personnel, which shall include analysis of blind QC check samples, when deemed appropriate;
- ⇨ Participation in in-house seminars on analytical methodologies and procedures;
- ⇨ Participation in job related seminars outside of the laboratory; and
- ⇨ Participation in conventions and meetings, i.e., ACS, etc.

u) Ethics policy statement developed by the laboratory and processes/procedures for educating and training personnel in their ethical and legal responsibilities including the potential punishments and penalties for improper, unethical, or illegal actions;

A vital part of ECI's analytical laboratory services is their Laboratory Ethics Training Program. An effective program starts with an Ethics Policy Statement that is supported by all staff, and is reinforced with initial and ongoing ethics training.

"It shall be the policy of ECI to conduct all business with integrity and in an ethical manner. It is a basic and expected responsibility of each staff member and manager to hold to the highest ethical standard of professional conduct in the performance of all duties."

A proactive ethics training program is the most effective means of deterring and detecting improper, unethical, or illegal actions in the laboratory. There are six facets to the program: (1) clearly define improper, unethical, and illegal actions; (2) outline elements of prevention and detection programs for improper, unethical, or illegal actions; and (3) identify examples of inappropriate (i.e., potentially fraudulent) laboratory practices; (4) Annual Ethics and Data Integrity Training to be documented and maintained in the personnel file of each employee., (5) Documented training on new revisions of the Quality Systems Manual (QSM) and for new employees as needed. (6) Signed Ethics and Data Integrity Agreement (to be completed for new employees and annually thereafter)

Definition of Improper, Unethical, and Illegal Actions

Improper actions are defined as deviations from contract-specified or method-specified analytical practices and may be intentional or unintentional.

Unethical or illegal actions are defined as the deliberate falsification of analytical or quality assurance results, where failed method or contractual requirements are made to appear acceptable.

Prevention of laboratory improper, unethical, or illegal actions begins with a zero-tolerance philosophy established by management. Improper, unethical, or illegal actions are detected through the implementation of oversight protocols.

Prevention and Detection Program for Improper, Unethical, or Illegal Actions

ECI management has implemented a variety of proactive measures to promote prevention and detection of improper, unethical, or illegal activities. The following components constitute the basic program:

- ⇨ Data Integrity Standard Operating Procedure (SOP) T065
- ⇨ Data Integrity Documentation Procedures
- ⇨ An Ethics and Data Integrity Agreement that is read and signed by all personnel;
- ⇨ Initial and annual ethics training;

- ⇨ Internal audits;
- ⇨ Inclusion of anti-fraud language in subcontracts;
- ⇨ Analyst notation and sign-off on manual integration changes to data;
- ⇨ Active use of electronic audit functions when they are available in the instrument software; and
- ⇨ A "no-fault" policy that encourages laboratory personnel to come forward and report fraudulent activities. Alternately, employees may report ethics violations to a third party agent contracted by Eurofins USA c/o reports@lighthouse-services.com/eurofinsus

A proactive, "beyond the basics" approach to the prevention of improper, unethical, or illegal actions are a necessary part of laboratory management. As such, in addition to the requirements above, ECI has a designated ombudsman (data integrity officer) to whom laboratory personnel can report improper, unethical, or illegal practices, or provide routine communication of training, lectures, and changes in policy intended to reduce improper, unethical, or illegal actions.

Examples of Improper, Unethical, or Illegal Practices

Documentation that clearly shows how all analytical values were obtained are maintained by ECI and supplied to the data user as needed. To avoid miscommunication, ECI clearly documents all errors, mistakes, and basis for manual integrations within the project file and case narrative as applicable. Notification is also made to the appropriate supervisor so that appropriate corrective actions can be initiated. Gross deviations from specified procedures are investigated for potential improper, unethical, or illegal actions, and findings of fraud are fully investigated by senior management. Examples of improper, unethical, or illegal practices are identified below:

- ⇨ Improper use of manual integrations to meet calibration or method QC criteria (for example, peak shaving or peak enhancement are considered improper, unethical, or illegal actions if performed solely to meet QC requirements);
- ⇨ Intentional misrepresentation of the date or time of analysis (for example, intentionally resetting a computer system's or instrument's date and/or time to make it appear that a time/date requirement was met);
- ⇨ Falsification of results to meet method requirements;
- ⇨ Reporting of results without analyses to support (i.e., dry-labbing);
- ⇨ Selective exclusion of data to meet QC criteria (for example, initial calibration points dropped without technical or statistical justification);
- ⇨ Misrepresentation of laboratory performance by presenting calibration data or QC limits within data reports that are not linked to the data set reported, or QC control limits presented within QAPP that are not indicative of historical laboratory performance or used for batch control;
- ⇨ Notation of matrix inference as basis for exceeding acceptance limits (typically without implementing corrective actions) in interference-free matrices (for example, method blanks or laboratory control samples);
- ⇨ Unwarranted manipulation of computer software (for example, improper background subtraction to meet ion abundance criteria for GC/MS tuning, chromatographic baseline manipulations);
- ⇨ Improper alteration of analytical conditions (for example, modifying EM voltage, changing GC temperature program to shorter analytical run time) from standard analysis to sample analysis;
- ⇨ Misrepresentation of QC samples (for example, adding surrogates after sample extraction, omitting sample preparation steps for QC samples, over- or under-spiking); and
- ⇨ Reporting of results from the analysis of one sample for those of another.

v) Reference to procedures for reporting analytical results;

Standard operating procedures pertaining to the reporting of results are available to all laboratory personnel. They are: SOP-T009, Significant Figures, Rounding, and Reporting of Results; SOP-T025, Reporting of Tentatively Identified Compounds (TICs); and T-026, Reporting of Data Qualifiers.

All analytical data generated within ECI is thoroughly checked for accuracy and completeness. The data validation process consists of data generation, reduction, and four levels of review as described below.

The analyst generating the analytical data has the primary responsibility for its correctness and completeness. All data is generated and reduced following protocols specified in the appropriate SOPs. Each analyst reviews the quality of his or her work based upon an established set of guidelines specified in the SOPs or as specified by project requirements. The analyst reviews the data package to ensure that:

- ⇨ Holding times have not been exceeded;
- ⇨ Sample preparation information is correct and complete;
- ⇨ Analysis information is correct and complete;
- ⇨ The appropriate procedures were employed;
- ⇨ Analytical results are correct and complete;
- ⇨ All associated QC is within established control limits and, if not, out-of-control forms are completed thoroughly explaining the cause and corrective action taken;
- ⇨ Any special sample preparation and analytical requirements have been met; and
- ⇨ Documentation is complete, i.e., all anomalies in the preparation and analysis have been documented; out-of-control forms, if required, are complete, etc.

The data reduction and validation steps are documented, signed, and dated by the analyst on the QC Review coversheet accompanying each data package. This initial review step, performed by the analyst, is designated as primary review. The analyst then forwards the data package to his or her Group Leader, or designated data reviewer, who performs a secondary review. Secondary reviews consist of an independent check equivalent to that of the primary review and are designed to ensure that:

- ⇨ Calibration data is scientifically sound, appropriate to the method, and completely documented;
- ⇨ QC data is within established guidelines or reported with appropriate clarification/qualification;
- ⇨ Qualitative identification of sample components is correct;
- ⇨ Quantitative results are correct;
- ⇨ Documentation is complete and any anomalies properly addressed and documented;
- ⇨ The data is ready for incorporation into the final report package; and
- ⇨ The data package is complete and ready for archiving.

A significant component of the secondary review is the documentation of any errors that have been identified and corrected during the review process. ECI believes that the data package that is submitted for a secondary review should be free from errors. Errors that are discovered are documented and formally transmitted to the appropriate Group Leader. The cause of the errors is then addressed by additional training or clarification of procedures (SOP revisions) to ensure that similar errors do not recur and high quality data will be generated.

Signature of Data Reviewer and the date of review document the completion of secondary reviews on the QC Review coversheet. These constitute approval for data release and generation of analytical report.

During both of the QC review processes, 100% of the raw data associated with the entire project is available to the reviewer. Data packages are checked back to the raw data as deemed necessary by the reviewer.

Following draft report generation, the report is reviewed by the Project Manager to ensure that the data set and quality control data is complete and meets the specific requirements of the project. When available, the data is also evaluated against historical site information. Once all requested analytical work has been verified as complete, a final report is generated and signed by the Project Manager.

Following approval for release by the Project Manager, the Quality Assurance Manager or other qualified personnel may review 10% of the project files back to the raw data as an additional check, if a situation so warrants.

A variety of reporting formats, from Portable Document File (PDF), normal typed reports to computerized data tables to complex reports discussing regulatory issues are available. In general, ECIreports contain the following information.

Analytical Data

Analytical data is reported by sample identification (both client and laboratory) and test. Pertinent information including date(s) sampled, received, prepared, and analyzed; any required data qualifiers are included on each results page. The reporting limit for each method analyte is also listed. Additional data may include Method Detection Limits (MDLs).

QC Data

A QC Summary is provided with each final report. Unless otherwise specified in a QAPP or requested by the client, QC Summaries include results for method blanks, matrix spikes, matrix spike duplicates, and surrogate spikes. Laboratory control sample and method blank surrogates are routinely included if matrix interference results in a QC outlier. The effective control limits for the reported QC values are also provided on the QC Summary as well as explanations for any QC outliers. Case Narratives may be included as appropriate.

As required for the project, data reports from “results only” through “full CLP-like” will be generated and provided. Included in this range are reports for the major DOD/DOE programs including NFESC, AFCEE, and USACE.

Methodology

References for the preparative and analytical methodology employed is included on all preliminary or final analytical reports.

Signatory

Final reports are ready for release to the client following review and approval by the Project Manager, as evidenced by his/her signature on the final report cover page. An approved signatories listing shall be maintained by the QA office.

Preliminary Data

Upon client request, preliminary data shall be released prior to completion of a full QC review. Preliminary data is subject to change pending QC review and, therefore, shall be clearly marked as “Preliminary”. This qualification is provided as notification to the client that the data review process has not been completed yet and that the data is subject to possible modification resulting therefrom.

Revised Data

Analytical reports that have been revised for any reason from the original sent report shall be noted as being revised with a report note, case narrative or indication as to the revision.

Formatting

At a minimum, an analytical report shall consist of the Report Cover Page, Analytical Results, QA/QC Data (Default), Footnotes/Comments Page, Sample Receipt Form and COC. Paginated reports shall be employed for all reports unless used for non-NELAP analysis.

w) A Table of Contents and applicable lists of references and glossaries, and appendices.

FIGURE 1:

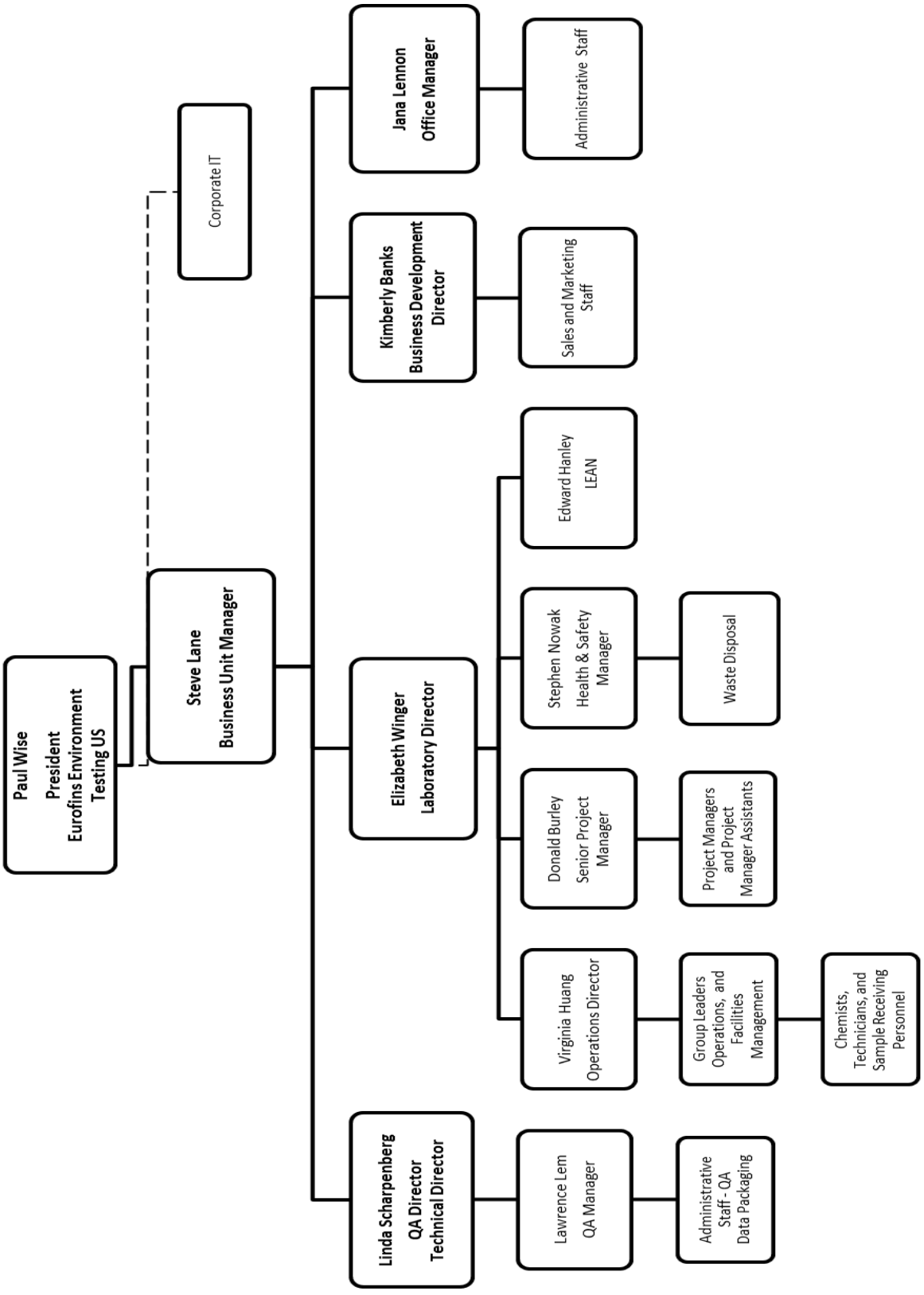
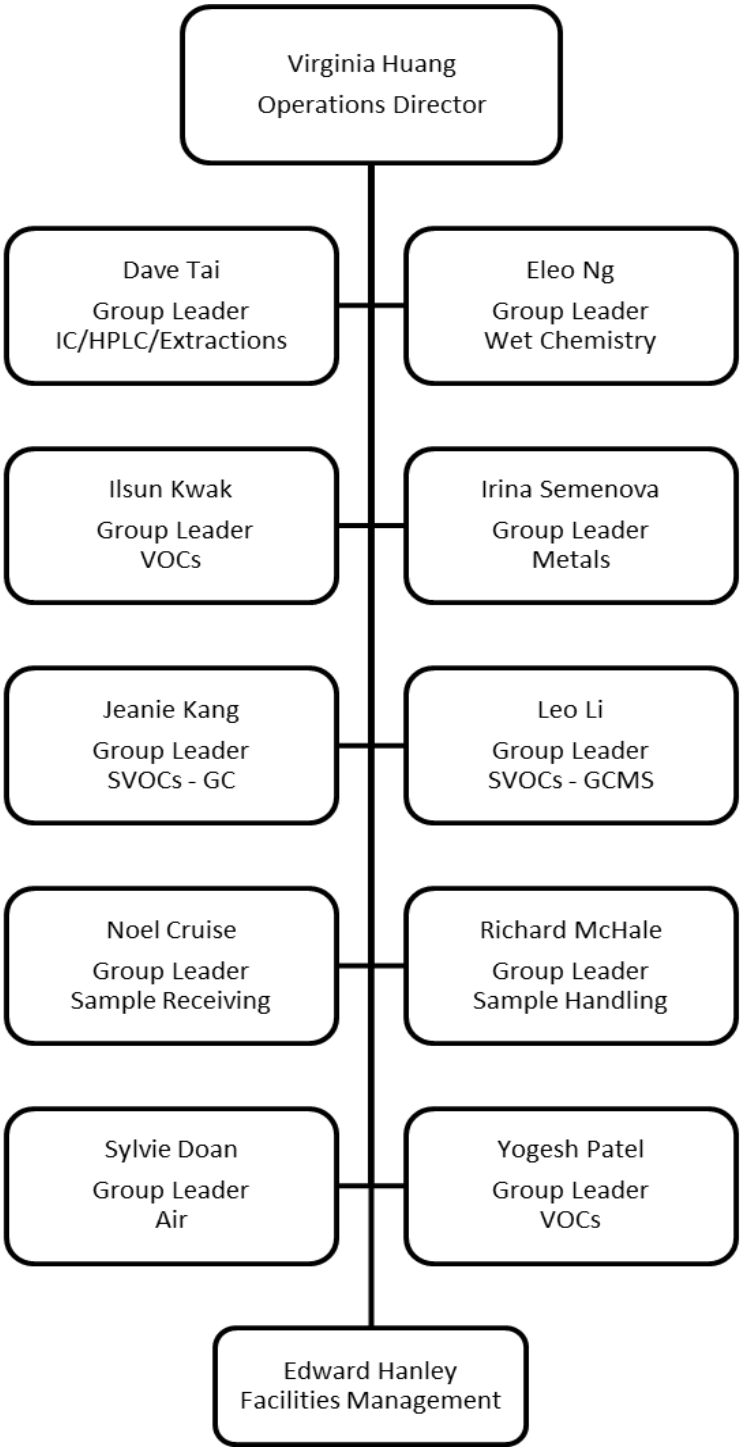

Paul Wise
President
Eurofins Environment Testing US
Steve Lane
Business Unit Manager
Corporate IT
Jana Lennon
Office Manager
Administrative Staff
Kimberly Banks
Business Development Director
Sales and Marketing Staff
Elizabeth Winger
Laboratory Director
Edward Hanley
LEAN
Stephen Nowak
Health & Safety Manager
Waste Disposal
Donald Burley
Senior Project Manager
Project Managers and Project Manager Assistants
Virginia Huang
Operations Director
Group Leaders Operations, and Facilities Management
Chemists, Technicians, and Sample Receiving Personnel
Linda Scharpenberg
QA Director
Technical Director
Lawrence Lem
QA Manager
Administrative Staff - QA Data Packaging

FIGURE 2:


Virginia Huang
Operations Director
Dave Tai
Group Leader
IC/HPLC/Extractions
Eleo Ng
Group Leader
Wet Chemistry
Ilsun Kwak
Group Leader
VOCs
Irina Semenova
Group Leader
Metals
Jeanie Kang
Group Leader
SVOCs - GC
Leo Li
Group Leader
SVOCs - GCMS
Noel Cruise
Group Leader
Sample Receiving
Richard McHale
Group Leader
Sample Handling
Sylvie Doan
Group Leader
Air
Yogesh Patel
Group Leader
VOCs
Edward Hanley
Facilities Management

5.3 Audits

5.3.1 Internal Audits

The laboratory arranges comprehensive annual internal audits to verify that its operations continue to comply with the requirements of the laboratory's said quality system. The Quality Assurance Manager or the Quality Assurance Assistant plans and organizes audits as required by a predetermined schedule and requested by management. The internal audits are buttressed by regular and scheduled Test Method Assessments (TMA).

The Quality Assurance Assistant or other qualified personnel, independent of the activity to be audited, will carry out such audits following the procedures noted in SOP T028, Internal Audit Procedures.

Personnel do not audit their own activities except when it can be demonstrated that an effective audit will be carried out.

Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, the laboratory takes immediate corrective action and immediately notifies, in writing, any client whose work was involved.

i. List of available qualified personnel for internal audits include:
   - QA Director
   - QA Manager
   - QA Assistant
   - Department Manager
   - Assistant Department Manager
   - Group Leader (For departments other than their own)
   - Program Manager
   - Health and Safety Manager (For non-analytical departments)
   - Any Senior Chemist (With documented training in proper internal auditing procedures from a qualified source).

ii. The minimum qualifications for an internal auditor shall be:
   - Education: A Bachelors (BS) Degree in an applied science with 16 semester hours in chemistry.
   - Experience: Two years' experience in an instrumental analytical technique for environmental analysis of representative environmental samples. Training to the most current revision of ECISOP T028 (Internal Audits). The training to be overseen by an individual that is ISO 17025 / 9001 trained in internal auditing procedures, or equivalent.
   - An advanced (MS, PhD.) degree may be substituted for one year of experience.

Any outside audit findings will also be included in the Internal Audits.

5.3.2 Management Review

ECI management conducts an annual review of its quality system and its testing and calibration activities to ensure its continuing suitability and effectiveness and to introduce any necessary changes or improvements in the quality system and laboratory operations.

This review takes account of reports from managerial and supervisory personnel, the outcome of recent internal audits, assessments by external bodies, the results of inter-laboratory comparisons or proficiency tests, any changes in the volume and type of work undertaken, feedback from clients, senior lab personnel, corrective actions, and other relevant factors.

The laboratory shall have a procedure for review by management, and maintain records of review findings and actions. For more detailed descriptions Reference section 18.1 of this QSM and SOP T030.

5.3.3 Audit Review

All audit and review findings and any corrective actions that arise from them are documented. The laboratory management ensures that these actions are discharged within the agreed time frame as indicated in the quality manual and/or SOPs.

5.3.4 Performance Audits

In addition to periodic audits, the laboratory ensures the quality of results provided to clients by implementing checks to monitor the quality of the laboratory's analytical activities. Examples of such checks are:

a) Internal quality control procedures using statistical techniques (see Section 5.4 below);

b) Participation in proficiency testing or other inter-laboratory comparisons;

c) Use of certified reference materials and/or in-house quality control using secondary reference materials as specified in ECIQSM Section 5.4;

d) Replicate testing using the same or different test methods;

g) Re-testing of retained samples;

h) Correlation of results for different but related analysis of a sample (for example, total phosphorus should be greater than or equal to orthophosphate).

5.3.5 Corrective / Preventive Actions

a) In addition to providing acceptance criteria and specific protocols for corrective/preventive actions in SOP-T022, the laboratory implements general procedures to be followed to determine when departures from documented policies, procedures and quality control have occurred. These procedures include but are not limited to the following:

    1) Identify the individual(s) responsible for assessing each QC data type;

    2) Identify the individual(s) responsible for initiating and/or recommending corrective/preventive actions;

    3) Define how the analyst shall treat a data set if the associated QC measurements are unacceptable;

    4) Specify how out-of-control situations and subsequent corrective actions are to be documented; and

    5) Specify procedures for management (including the QA officer) to review corrective/preventive action reports.

b) To the extent possible, sample results are reported only if all quality control measures are acceptable. If a quality control measure is found to be out of control, and the data are to be reported, all samples associated with the failed quality control measure are reported with the appropriate data qualifier(s).

5.4 Essential Quality Control Procedures

These general quality control principles apply, where applicable, to all testing at ECI. The manner in which each is implemented is dependent on the types of tests performed by the laboratory and is further described in Appendix D and in SOP-T020, Internal Quality Control Checks. The standards for any given test type assures that the applicable principles are addressed:

a) All laboratories have detailed written protocols in place to monitor the following quality controls:

   1) Positive and negative controls (blanks, spikes, reference toxicants, etc.) to monitor tests;

   2) Tests to define the variability and/or repeatability of the laboratory results such as replicates;

   3) Measures to assure the accuracy of the test method including calibration and/or continuing calibrations, use of certified reference materials, proficiency test samples, or other measures;

   4) Measures to evaluate test method capability, such as detection limits and quantitation limits or range of applicability such as linearity;

   5) Selection of appropriate formulae to reduce raw data to final results such as regression analysis, comparison to internal/external standard calculations, and statistical analyses;

   6) Selection and use of reagents and standards of appropriate quality;

   7) Measures to assure the selectivity of the test for its intended purpose; and

   8) Measures to assure constant and consistent test conditions (both instrumental and environmental) where required by the test method, such as temperature, humidity, light or specific instrument conditions.

b) All quality control measures are assessed and evaluated on an on-going basis, and quality control acceptance criteria are used to determine the usability of the data. (See Appendix D.)

c) The laboratory has procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exist. (See ECI QSM Section 11.2, Sample Acceptance Policy.)

d) The quality control protocols specified in the method manual (ECI QSM Section 10.1.2) is followed. ECI ensures that the essential standards outlined in NELAC 5, Appendix D, or mandated methods or regulations (whichever are more stringent) are incorporated into the method manuals. When it is not apparent which is more stringent the QC in the mandated method or regulations is to be followed.

   The essential quality control measures for testing are found in Appendix D.

6.0 PERSONNEL

6.1 General Requirements for Laboratory Staff

ECI's testing departments have a sufficient level of personnel with the necessary education, training, technical knowledge and experience to perform the assigned functions.

All personnel are responsible for complying with all quality assurance/quality control requirements that pertain to their organizational/technical function. Each technical staff member must have a combination of experience and education to adequately demonstrate a specific knowledge of their particular function and a general knowledge of laboratory operations, test methods, quality assurance/quality control procedures and records management.

6.2 Laboratory Management Responsibilities

In addition to ECI QSM Section 4.2.d, the laboratory management:

a) Defines the minimum level of qualification, experience and skills necessary for all positions in the laboratory. In addition to education and/or experience, basic laboratory skills such as using a balance and quantitative techniques, are considered.

b) Ensures that all technical laboratory staff members demonstrate capability in the activities for which they are responsible. Such demonstration is documented (See Appendix C). Note: In departments with specialized "work cells" (a well-defined group of analysts that together perform the method analysis), the group as a unit meets the above criteria and this demonstration is fully documented.

c) Ensures that the training of each member of the technical staff is kept up-to-date (on-going) by the following:

    1) Keeping evidence on file that demonstrates that each employee has read, understood, and is using the latest version of the laboratory's in-house quality documentation that relates to his/her job responsibilities.

    2) Documenting training courses or workshops on specific equipment, analytical techniques, or laboratory procedures.

    3) Documenting employee attendance at training courses on ethical and legal responsibilities including the potential punishments and penalties for improper, unethical or illegal actions. Keeping on file evidence that demonstrates that each employee has read, acknowledges, and understands their personal ethical and legal responsibilities including the potential punishments and penalties for improper, unethical or illegal actions.

    4) Maintains up-to-date analyst training records that contain a certification that technical personnel have read, understood and agreed to perform the most recent version of the test method (the approved method or SOP as defined by the laboratory document control system, ECI QSM Section 5.2.d) and documentation of continued proficiency by at least one of the following once per year:

        i. Acceptable performance of a blind sample (single blind to the analyst);

        ii. Another demonstration of capability;

        iii. Successful analysis of a blind performance sample on a similar test method using the same technology (e.g., GC/MS volatiles by purge and trap for Methods 524.2, 624, or 5035/8260) would only require documentation for one of the test methods;

        iv. At least four consecutive laboratory control samples with acceptable levels of precision and accuracy;

        v. If subsections i-iv cannot be performed, analysis of authentic samples with results statistically indistinguishable from those obtained by another trained analyst.

d) Documents all analytical and operational activities of the laboratory;

e) Supervises all personnel employed by the laboratory;

f) Ensures that all sample acceptance criteria (ECI QSM Section 11.0) are verified and that samples are logged into the sample tracking system and properly labeled and stored.

g) Documents the quality of all data reported by the laboratory.

h) Develops a proactive program for the prevention and detection of improper, unethical, or illegal actions. Components of this program could include: internal proficiency testing (single and double blind); post-analysis electronic and magnetic tape audits; effective reward program to improve employee vigilance and co-monitoring; and separate SOPs identifying appropriate and inappropriate laboratory and instrument manipulation practices.

6.2.1 Ownership Transfer / Out of Business

a) In the event that the laboratory transfers ownership or goes out of business, ECI will ensure that the records are maintained or transferred according to client instruction.

b) Upon ownership transfer, record retention requirements shall be addressed in the ownership transfer agreement and the responsibility for maintaining archives will be clearly established. In cases of bankruptcy, appropriate regulatory and state legal requirements concerning laboratory records will be followed.

c) In the event that the laboratory goes out of business, all records will revert to the control of the client or regulatory agency, as applicable. As much notice as possible will be given to clients and the accrediting bodies who have worked with the laboratory during the previous 5 years of such action.

6.3 Personnel Records

Records on the relevant qualifications, training, skills and experience of the technical personnel are maintained by the laboratory (see EC IQSM Section 6.2.c), including records on demonstrated proficiency for each laboratory test method, such as the criteria outlined in ECI QSM Section 10.5 for chemical testing.

7.0 PHYSICAL FACILITIES – ACCOMMODATION AND ENVIRONMENT

7.1 Environment

a) Laboratory accommodations, test areas, energy sources, lighting, heating and ventilation are such that they facilitate proper performance of tests.

b) The environment in which these activities are undertaken does not invalidate the results or adversely affect the required accuracy of the measurements. Particular care shall be taken when such activities are undertaken at sites other than the permanent laboratory premises.

c) The laboratory shall provide for the effective monitoring, control and recording of environmental conditions as appropriate. Such environmental conditions may include biological sterility, dust, electromagnetic interference, humidity, main voltage, temperature, and sound and vibration levels.

d) In instances where monitoring or control of any of the above-mentioned items is specified in a test method or by regulation, the laboratory meets and documents adherence to the laboratory facility requirements.

7.2 Work Areas

a) There is effective separation between neighboring areas when the activities therein are incompatible including volatile organic chemicals handling areas.

b) Access to and use of all areas affecting the quality of these activities are defined and controlled.

c) Adequate measures are taken to ensure good housekeeping in the laboratory and to ensure that any contamination does not adversely affect data quality.

d) Workspaces are available to ensure an unencumbered work area. Work areas include:

   1) Access and entryways to the laboratory;

   2) Sample receipt areas;

   3) Sample storage areas;

   4) Chemical and waste storage areas; and

   5) Data handling and storage areas.

8.0 EQUIPMENT AND REFERENCE MATERIALS

a) ECI is furnished with all items of equipment (including reference materials) required for the correct performance of tests for which accreditation is maintained. Note that ECI does not use equipment outside its permanent control.

b) All equipment is properly maintained, inspected, and cleaned. Maintenance procedures are documented.

c) Any equipment item that has been subjected to overloading or mishandling, or that gives suspect results, or has been shown by verification or otherwise to be defective, is taken out of service, clearly identified and wherever possible stored at a specified place until it has been repaired and shown by calibration, verification or test to perform satisfactorily. The laboratory shall examine the effect of this defect on previous calibrations or tests.

d) When appropriate, each item of equipment, including reference materials, is labeled, marked, or otherwise identified to indicate its calibration status.

e) Records are maintained of each major item of equipment and all reference materials significant to the tests performed. These records include documentation on all routine and non-routine maintenance activities in assigned log books and reference material verifications.

   The records include:

   1) The name of the item of equipment;

   2) The manufacturer's name, type identification, and serial number or other unique identification;

   3) Date received and date placed in service (if available);

   4) Current location, where appropriate;

5) If available, condition when received (e.g., new, used, reconditioned);

6) Copy of the manufacturer's instructions, where available;

7) Dates and results of calibrations and/or verifications and date of the next calibration and/or verification;

8) Details of maintenance carried out to date and planned for the future; and

9) History of any damage, malfunction, modification or repair.

9.0 MEASUREMENT TRACEABILITY AND CALIBRATION

9.1 General Requirements

All measuring operations and testing equipment having an effect on the accuracy or validity of tests are calibrated and/or verified before being put into service and on a continuing basis. The laboratory has an established program for the calibration and verification of its measuring and test equipment. This includes balances, thermometers and control standards.

9.2 Traceability of Calibration

a) The overall program of calibration and/or verification and validation of equipment is designed and operated so as to ensure that measurements made by the laboratory are traceable to national standards of measurement.

b) Calibration certificates indicate the traceability to national standards of measurement and provide the measurement results and associated uncertainty of measurement and/or a statement of compliance with an identified metrological specification. The laboratory maintains records of all such certification in the QA office.

c) Where traceability to national standards of measurement is not applicable, the laboratory provides satisfactory evidence of correlation of results, for example, by participation in a suitable program of inter-laboratory comparisons, proficiency testing, or independent analysis.

9.3 Reference Standards

a) Reference standards of measurement held by the laboratory (such as Class S or equivalent weights, or traceable thermometers) are used for calibration only and for no other purpose, unless it can be demonstrated that their performance as reference standards has not been invalidated. A body that can provide traceability calibrates reference standards of measurement. Where possible, this traceability is to a national standard of measurement.

b) There is a program of calibration and verification for reference standards.

   i. Two weeks prior to their date of calibration expiration, individual thermometers are removed from service and replaced by newly calibrated units from the supplier.

   ii. ECI keeps two sets of Class S weights on hand for use in the laboratory. One set is used for daily calibration checks, and the second set is kept for back up use should the first set be damaged, lost or otherwise compromised. The second set of weights is also place in service when the daily use set is shipped off site for recalibration.

iii. Analytical balances are serviced and calibrated on a routine, annual schedule.

c) Where relevant, reference standards and measuring and testing equipment are subjected to in-service checks between calibrations and verifications. Reference materials are traceable. Where possible, traceability is to national or international standards of measurement, or to national or international standard reference materials.

d) NIST-Traceable Weights and Thermometers

i. Reference standards of measurement shall be used for the purposes of calibration only. NIST traceable thermometers and NIST-traceable weights shall not be used for routine testing. If NIST traceable reference sources are used for routine testing they shall not be used for calibration purposes unless it can be shown that their performance as reference standards would not be invalidated.

ii. For NIST-traceable weights and thermometers, ECI requires that all calibrations be conducted by a calibration laboratory accredited by ACLASS, A2LA or other recognized accrediting body.

a. The calibration laboratory must hold ISO 17025 or ISO 9001 accreditation for the services rendered. Prior to use, QA verifies that the selected vendor holds the appropriate scope of accreditation for the services required.

b. The calibration certificate or report supplied by the calibration laboratory must contain a traceability statement, the conditions under which the calibrations were made, a compliance statement with an identified metrological specification and the pertinent clauses when applicable, and a clearly identified record of the quantities and functional test results before and after re-calibration.

c. The certificate and scope of accreditation is kept on file at the laboratory and is reviewed yearly.

iii. If significant amendments are made to a calibration certificate, it must have its own unique report identifier and must reference the one it is replacing. The piece of equipment must be identified in the amended report using its unique serial number or other laboratory defined identifier. The amended report is maintained with the original calibration report.

iv. Laboratory balances are recalibrated annually by an external, certified vendor that is certified to ISO 17025 / ISO 9001 standards for calibration. Prior to use, QA verifies that the selected vendor holds the appropriate scope of accreditation for the services required. This service is documented on each balance with a signed and dated certification sticker.

v. NIST mercury thermometers are sent out for recalibration every five years, or are replaced. All working mercury thermometers are calibrated annually against a NIST-traceable reference thermometer. All digital temperature measuring devices (min/max thermometers, IR guns) are calibrated quarterly. Equipment that does not meet acceptance criteria is removed from service and repaired or replaced. Calibration reports are maintained by the QA Manager

vi. Balance calibrations and temperature readings of ovens, refrigerators, and incubators are checked on each day of use. Min/Max thermometers are used for refrigerators and freezers to continually monitor temperature performance.

e) Traceable Reference Standards and Materials

i. Reference standards and materials are traceable to certified reference materials, where available. Commercially prepared standard materials are purchased from vendors accredited by A2LA, NVLAP (National Voluntary Lab Accreditation Program) or other recognized vendor, and come with a Certificate of Analysis that documents the purity of the standard and expiration date, if assigned. If a standard cannot be purchased from a vendor that supplies a Certificate of Analysis, the purity of the standard is documented by analysis against a known reference.

ii. Analytical reagents must be at a minimum the purity required by or stated in the test method. Commercial materials that are purchased for the preparation of calibration, verification or spiking solutions, are usually accompanied by an assay certificate or the purity is noted on the label. If the purity is ≥96%, the weight provided by the vendor may be used without correction. If the purity is <96%, a correction will be made to solution concentrations prepared from that material.

iii. The receipt of all reference standards and materials, including received date and expiration date, is documented by the laboratory at the time of receipt, in chemical receiving logbooks. All documentation received with the reference standard or material (Certificate of Analysis or Purity Certificates) is retained by the laboratory. To prevent contamination and/or deterioration in quality, all standards and materials are handled and stored according to the method or manufacturer's requirements.

iv. Preparation of standard or reference materials are documented in Standard Preparation Logbooks maintained in each department. These records show the traceability to the purchased standards or materials, and include the method of preparation, date of preparation, expiration date, and preparer's initials, at a minimum. Reference standards are assigned a unique identifier and are then labeled with the identifier and expiration date. Refer to ECISOP, T003, Standards and Reagents Login, Preparation, Storage and Disposal, for additional information.

v. All standards, reference, primary and working, whether purchased from a commercial vendor or prepared by the laboratory, must be checked regularly to ensure that the variability of the standard from the 'true' value does not exceed method requirements. Calibration standards are checked by comparison with a standard from a second source, usually another manufacturer and vendor. In cases where a second manufacturer is not available, a different lot, with vendor certification, may be used as a second source.

vi. Quality control (QC) criteria for primary and second source standards are defined in laboratory SOPs. The Reagent and Chemicals SOP, T107, gives a general overview of the requirements with the determinative SOPs for each process further defining the QC acceptance criteria. In most cases, the analysis of an Initial Calibration Verification (ICV) or LCS/LCSD (where there is no sample preparation) is used as the second source verification of a primary calibration source.

9.4 Calibration

Calibration requirements are divided into two parts: (1) requirements for analytical support equipment, and (2) requirements for instrument calibration. In addition, the requirements for instrument calibration are divided into initial calibration and second source or initial calibration verification, and continuing calibration verification.

9.4.1 Support Equipment

These standards apply to all devices that may not be the actual test instrument, but are necessary to support laboratory operations. These include but are not limited to: balances, ovens, refrigerators, freezers, incubators, water baths, thermometers, and volumetric dispensing devices (such as Eppendorf®, or automatic dilutor/dispensing devices) if quantitative results are dependent on their accuracy, as in standard preparation and dispensing or dilution into a specified volume.

a) All support equipment is maintained in proper working order. The records of all repair and maintenance activities, including service calls is kept.

b) All support equipment is calibrated or verified at least annually, using NIST traceable references when available, over the entire range of use. The results of such calibration are within the specifications required of the application for which this equipment is used or:

   1) The item is removed from service until repaired; or

   2) The laboratory maintains records of established correction factors to correct all measurements.

c) Raw data records are retained to document equipment performance.

d) Prior to use on each working day, balances, ovens, refrigerators, freezers, and water baths are checked in the expected use range, with NIST traceable calibrated references. The acceptability for use or continued use is according to the needs of the analysis or application for which the equipment is being used.

e) Mechanical volumetric dispensing devices including burettes (except Class A glassware) are checked for accuracy on at least a quarterly use basis. Glass microliter syringes are to be considered Class A glassware, and come with a certificate from the manufacturer attesting to established accuracy or the accuracy is initially demonstrated and documented by the laboratory.

9.4.2 Instrument Calibration

This manual specifies the essential elements that define the procedures and documentation for initial instrument calibration and continuing instrument calibration verification to ensure that the data are of known quality and be appropriate for a given regulation or decision. This manual does not specify detailed procedural steps ("how to") for calibration, but establishes the essential elements for selection of the appropriate technique(s). This approach allows flexibility and permits the employment of a wide variety of analytical procedures and statistical approaches currently applicable for calibration. If more stringent standards or requirements are included in a mandated test method or by regulation, the laboratory demonstrates that such requirements are met. If it is not apparent which standard is more stringent, then the requirements of the regulation or mandated test method are to be followed.

Note: In the following sections, initial instrument calibration is directly used for quantitation and continuing instrument calibration verification is used to confirm the continued validity of the initial calibration, unless otherwise stipulated by the analytical method.

9.4.2.1 Initial Instrument Calibrations

The following items are essential elements of initial instrument calibration:

a) The details of the initial instrument calibration procedures including calculations, integrations, acceptance criteria and associated statistics are included or referenced in the test method SOP. When initial instrument calibration procedures are referenced in the test method, the referenced material is retained by the laboratory and is available for review.

b) Sufficient raw data records are retained to permit reconstruction of the initial instrument calibration, e.g., calibration date, test method, instrument, analysis date, each analyte name, analyst's initials or signature; concentration and response, calibration curve or response factor; or unique equation or coefficient used to reduce instrument responses to concentration.

c) Sample results are quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification unless specifically stated in a mandated test method.

d) All initial instrument calibrations are verified with a standard obtained from a second manufacturer or lot. Traceability shall be to a national standard, when available.

e) Criteria for the acceptance of an initial instrument calibration is established, e.g., correlation coefficient or relative percent difference. The criteria used are appropriate to the calibration technique employed.

f) Results of samples not bracketed by initial calibration standards (within calibration range) are reported as having less certainty, e.g., defined qualifiers or flags or explained in the case narrative. As determined by the method, the lowest calibration standard is at or above the method detection limit and at or below the reporting limit.

g) If the initial instrument calibration results are outside established acceptance criteria, corrective actions are performed. Data associated with an unacceptable initial instrument calibration is not reported.

h) Calibration standards include concentrations at or below the regulatory limit/decision level, if the laboratory knows these limits/levels, unless these concentrations are below the laboratory's demonstrated detection limits (See ECI QSM Section Appendix D.1.5 Detection Limits).

i) If a reference or mandated method does not specify the number of calibration standards, the minimum number is two, not including blanks or a zero standard. The laboratory's standard operating procedure defines the number of points for establishing the initial instrument calibration.

9.4.2.2 Continuing Instrument Calibration Verification

When an initial instrument calibration is not performed on the day of analysis, the validity of the initial calibration is verified prior to sample analyses by analyzing a continuing calibration verification standard with each analytical batch. The following items are essential elements of continuing calibration verification:

a) The details of the continuing calibration procedure, calculations and associated statistics must be included or referenced in the test method SOP.

b) A continuing calibration verification standard must be analyzed at the beginning and end of each analytical batch, and where required by method or project, at a specific frequency, every 10 or 20 samples or 12 hours, within the batch. The concentrations of the calibration verification shall be varied within the established calibration range. If an internal standard is used, only one continuing calibration verification standard must be analyzed, prior to sample or QC analysis, per analytical batch.

c) Sufficient raw data records must be retained to permit reconstruction of the continuing calibration verification, e.g., test method, instrument, analysis date, each analyte name, concentration and response, calibration curve or response factor, or unique equations or coefficients used to convert instrument responses into concentrations. Continuing calibration verification records must explicitly connect the continuing calibration verification data to the initial calibration.

d) Criteria for the acceptance of a continuing calibration verification must be established, e.g., relative percent difference.

e) If the continuing calibration verification results obtained are outside established acceptance criteria, corrective actions must be performed. If routine corrective action procedures fail to produce a second (consecutive and immediate) calibration verification within acceptance criteria, then the laboratory shall demonstrate performance after corrective action with two consecutive successful calibration verifications, or a new instrument calibration must be performed. If the laboratory has not demonstrated acceptable performance, sample analyses shall not occur until a new initial calibration curve is established and verified.

As an exception, sample data associated with an unacceptable continuing calibration verification may be reported as qualified data under the following special conditions:

i. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification are reanalyzed after a new calibration curve has been established, evaluated and accepted.

ii. When the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification are reanalyzed after a new calibration curve has been established, evaluated and accepted.

10.0 TEST METHODS AND STANDARD OPERATING PROCEDURES

10.1 Methods Documentation

a) The laboratory has documented instructions on the use and operation of all relevant equipment, on the handling and preparation of samples and for calibration and/or testing, where the absence of such instructions could jeopardize the calibrations or tests.

b) All instructions, standards, manuals, and reference data relevant to the work of the laboratory are maintained up-to-date and be readily available to the staff.

10.1.1 Standard Operating Procedures (SOPs) Administrative

ECI maintains standard operating procedures that accurately reflect all phases of current laboratory activities such as instrument operation, assessing data integrity, corrective actions, handling customer complaints, reporting of test results, etc.

a) These documents, for example, may be equipment manuals provided by the manufacturer or internally written documents.

b) The test methods may be copies of published methods as long as any changes or selected options in the methods are documented and included in the SOP (See 10.1.2.)

c) Copies of all SOPs are accessible to all personnel.

d) The SOPs are organized.

e) Each SOP clearly indicates the effective date of the document, the revision number and the signatures of the approving authorities.

10.1.2 Standard Operating Procedures (SOPs) Analytical

a) The laboratory has and maintains SOPs for each accredited analyte or test method.

b) This SOP may consist of copies of published or referenced test methods or standard operating procedures that have been written by the laboratory. In cases where modifications to the published method have been made by the laboratory or where the referenced test method is ambiguous or provides insufficient detail, these changes or clarifications are clearly described. Each test method includes or references where applicable:

1) Identification of the test method;
2) Applicable matrix or matrices;
3) Detection limit;
4) Scope and application, including components to be analyzed;
5) Summary of the test method;
6) Definitions;
7) Interferences;
8) Safety;
9) Equipment and supplies;
10) Reagents and standards;
11) Sample collection, preservation, shipment, and storage;
12) Quality control;
13) Calibration and standardization;
14) Procedure;
15) Calculations;
16) Method performance;
17) Pollution prevention;
18) Data assessment and acceptance criteria for quality control measures;
19) Corrective actions for out-of-control data;
20) Contingencies for handling out-of-control or unacceptable data;
21) Waste management;
22) References; and
23) Any tables, diagrams, flowcharts, and validation data.
24) Modifications
25) Revision History

Laboratory procedures other than preparative or analytical procedure may use a shortened format as outlined in SOP T001.

10.2 Exceptionally Permitting Departures from Documented Policies / Procedures

a) If it is necessary to depart from a documented procedure or policy due to circumstances outside of ECI's control or due to conditions encountered while preparing or analyzing a sample, the following will be documented.

    1) The nature of the exception
    2) How the data or procedure may be impacted
    3) Any Corrective Action that may be needed.
    4) Any approval from a client that may be required.
    5) Approval by management to report or proceed with the exception.
    6) A Case Narrative with the Final Report explaining the exception.

10.3 Test Methods

The laboratory uses appropriate test methods and procedures for all tests and related activities within its responsibility (including, as applicable, sample collection, sample handling, transport and storage, sample preparation and sample analysis). The method and procedures shall be consistent with the accuracy required, and with any standard specifications relevant to the calibrations or tests concerned.

a) When the use of specific test methods for a sample analysis is mandated or requested, only those methods are used.

b) Where test methods are employed that are not required, as in the Performance Based Measurement System approach, the methods are fully documented and validated (see ECIQSM Section 10.1.2 and Appendix C), and are available to the client and other recipients of the relevant reports.

10.4 Test Method Assessment

The laboratory will periodically conduct a Test Method Assessment (TMA) on the analytical methods in use. These TMAs will be conducted under the guidance of SOP T029. The purpose is to evaluate the compliance between bench performances of the method versus the current ECI Standard Operating Procedure versus the promulgated or published method. Discrepancies will need to be addressed and resolved. Note that some methods are totally prescriptive while others may contain prescriptive aspects, and still others are performance based. In many cases, modifications to the published method may be required due to circumstances outside the laboratories' control.

10.5 Demonstration of Capability

a) Prior to acceptance and institution of any test method, satisfactory demonstration of method capability is required. (See ECI QSM Section Appendix C and 6.2.b.) This demonstration does not test the performance of the method in real world samples, but in the applicable and available clean matrix (sample of a matrix is which no target analytes or interferences are present at concentrations that impact the results of a specific test method), e.g., water, solids and air. In addition, for analytes that do not lend themselves to spiking, the demonstration of capability may be performed using quality control samples.

b) Continuing demonstration of method performance, as per the quality control requirements in Appendix D (such as laboratory control samples) is required.

c) In all cases, the appropriate forms, such as the Certification Statement (Appendix C), is completed and retained by the laboratory to be made available upon request. The laboratory retains all associated supporting data necessary to reproduce the analytical results summarized in the Certification Statement. (See Appendix C for an example of a Certification Statement.)

d) Demonstration of capability is completed each time there is a significant change in instrument type, personnel, or test method.

e) In departments with specialized "work cell(s)" (a group consisting of analysts with specifically defined tasks that together perform the test method), the group as a unit must meet the above criteria and this demonstration of capability is fully documented.

f) When a work cell is employed, and the members of the cell change, the new employee(s) must work with an experienced analyst in that area of the work cell where they are employed. This new work cell must demonstrate acceptable performance through acceptable continuing performance checks (appropriate sections of Appendix D, such as laboratory control samples). Such performance is documented and the four preparation batches following the change in personnel must not result in the failure of any batch acceptance criteria, e.g., method blank and laboratory control sample, or the demonstration of capability must be repeated. In addition, if the entire work cell is changed or replaced, the new work cell must perform the demonstration of capability (Appendix C).

g) Performance of the work cell is linked to the training records of the individual members of the work cell (See ECI QSM Section 6.2).

10.6 Sample Aliquots

Where sampling (as in obtaining sample aliquots from a submitted sample) is carried out as part of the test method, the laboratory shall use documented procedures and appropriate techniques to obtain representative subsamples. Reference SOP M230, Homogenization and Compositing of Solid, Soil and Sediment Samples for further guidance.

10.7 Data Verification

Calculations and data transfers are subject to appropriate checks.

a) The laboratory has Standard Operating Procedures that ensure that the reported data are free from transcription and calculation errors.

b) The laboratory has Standard Operating Procedures that ensure that all quality control measures are reviewed, and evaluated before data are reported. Refer to SOPs T020, internal Quality Control Checks and T062, Project Management and Analytical Report Review

c) The laboratory has Standard Operating Procedures that address manual calculations including manual integrations. Refer to SOPs T065, Data Integrity and T023, Peak Integration Procedures.

10.8 Documentation and Labeling of Standards and Reagents

Documented procedures exist for the purchase, receipt and storage of consumable materials used for the technical operations of the laboratory.

a) The laboratory retains records for all standards, reagents and media including the manufacturer/vendor, the manufacturer's Certificate of Analysis or purity (if supplied), the date of receipt, recommended storage conditions, and an expiration date after which the material is not used, unless the laboratory verifies its suitability for testing use.

b) Original containers (such as those provided by the manufacturer or vendor) are labeled with an expiration date.

c) Records are maintained on reagent and standard preparation. These records indicate traceability to purchased stocks or neat compounds, reference to the method of preparation, date of preparation, expiration date and preparer's initials.

d) All containers of prepared reagents and standards bear a unique identifier and expiration date and are linked to the documentation requirements in ECIQSM Section 10.8.c above.

10.9 Computers and Electronic Data Related Requirements

Where computers, automated equipment, or microprocessors are used for the capture, processing, manipulation, recording, reporting, storage or retrieval of test data, ECI ensures that:

a) All requirements of the NELAC Standard (i.e., Chapter 5 of NELAC) are met;

b) Computer software is tested and documented to be adequate for use, e.g., internal audits, personnel training, focus point of QA and QC;

c) Procedures are established and implemented for protecting the integrity of data. Such procedures include, but are not limited to, integrity of data entry or capture, data storage, data transmission and data processing;

d) Computer and automated equipment are maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of calibration and test data; and,

e) It establishes and implements appropriate procedures for the maintenance of security of data including the prevention of unauthorized access to, and the unauthorized amendment of, computer records.

11.0 SAMPLE HANDLING, SAMPLE ACCEPTANCE POLICY AND SAMPLE RECEIPT

While ECI does not have control of field sampling activities, the following are essential to ensure the validity of the laboratory's data.

11.1 Sample Tracking

a) The laboratory has a documented system for uniquely identifying the items to be tested, to ensure that there can be no confusion regarding the identity of such items at any time. This system includes identification for all samples, subsamples and subsequent extracts and/or digestates. The laboratory assigns a unique identification (ID) code to each sample container received in the laboratory. (The use of container shape, size, or other physical characteristic, such as amber glass, or purple top, is not an acceptable means of identifying the sample.)

b) This laboratory code is maintained as an unequivocal link with the unique field ID code assigned each container.

c) The laboratory ID code is placed on the sample container as a durable label.

d) The laboratory ID code is entered into the laboratory records (see ECIQSM Section 11.3.d) and is the link that associates the sample with related laboratory activities such as sample preparation or calibration.

e) In cases where the sample collector and analyst is the same individual or the laboratory pre-assigns numbers to sample containers, the laboratory ID code may be the same as the field ID code.

11.2 Sample Acceptance Policy

The laboratory has a written sample acceptance policy that clearly outlines the circumstances under which samples are accepted or rejected. Data from any samples that do not meet the following criteria are flagged in an unambiguous manner, and the nature of the variation is clearly defined. The sample acceptance policy is available to sample collection personnel and includes, but is not limited to, the following areas of concern:

a) Proper, full, and complete documentation, that includes sample identification, the location, date and time of collection, collector's name, preservation type, sample type and any special remarks concerning the sample;

b) Proper sample labeling that includes a unique identification and a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink;

c) Use of appropriate sample containers;

d) Adherence to specified holding times;

e) Adequate sample volume. Sufficient sample volume must be available to perform the necessary tests; and,

f) Procedures to be used when samples show signs of damage, contamination or inadequate preservation.

g) Samples are NOT accepted if classified as extremely hazardous, reference section 5.2 k for examples.

11.3 Sample Acceptance Policy (Posted)

This sample acceptance policy outlines the circumstances in which received samples are accepted or rejected by Eurofins Calscience, Inc. (ECI). If any of the below criteria are not met, it may delay ECI's processing of samples, possibly compromising "short" holding time analyses. Where received

samples do not meet these criteria, ECI will contact the client. If immediate client contact cannot be made, and hold times are not an issue, samples will be appropriately stored until the situation is clarified with the client. If a delay in sample processing will result in missed holding times, and ECI deems there is sufficient information provided on the Chain-of-Custody (COC), the lab will proceed with sample log-in and processing; however, ECI will not assume any liability for samples processed under these circumstances.

Data from samples that do not meet the sample acceptance criteria are flagged and/or addressed in a case narrative, with the nature of the deviation clearly defined. Samples must have written authorization to proceed if not in compliance with this guidance.

1. Complete COC with the following information:

   Unique sample identification, date and time of collection, sample matrix, analysis requested, sampler's name, preservation type (if applicable), client name and address, any additional comments, signature of relinquishing party and date and time that samples were relinquished.

2. Sample temperature upon receipt of >0°C to 6°C, as applicable to the method.

   In the event that samples are collected on the same day that they are received by the laboratory, they are deemed acceptable if they are received on ice and the cooling process has begun.

3. Sample containers and preservatives must be appropriate for the test and method being requested on the COC.

4. Sample labels must include a unique identification written with indelible ink on water resistant labels that correspond with the COC.

5. Adequate sample volume must be provided for the analyses requested on the COC, and containers for volatile analyses must be free of headspace. This includes Tedlar bags and Summa canisters.

6. Sufficient holding time available to perform the analyses requested:

   Samples shall be received at the laboratory within 72 hours of sampling, or with at least 1/2 of the holding time left for the analysis, whichever is less. ECI always makes a best effort to ensure that holding times are not exceeded under these circumstances. In the event that a preparation or analysis is performed outside of the associated holding time, the data will be qualified in the report.

7. Coolers and samples must be received in good condition, with no obvious signs of damage or tampering.

8. Received with a copy of ECI's Foreign Soil Permit, if applicable.

9. Please note, mixed waste, or samples classified as extremely hazardous are **NOT** accepted.

If you require additional information or clarification, please do not hesitate to contact ECI, or your Project Manager at (714) 895-5494.

11.4 Sample Receipt Protocols

a) Upon receipt, the condition of the sample, including any abnormalities or departures from standard condition as prescribed in the relevant test method, is recorded. All items specified in ECIQSM Section 11.2 above are checked.

   1) All samples that require cold temperature preservation are considered acceptable if the arrival temperature is within 2°C of the required temperature or the method-specified range. For samples with a specified temperature of 4°C, samples with a temperature ranging from just above the freezing temperature of water to 6°C shall be acceptable. Samples that are hand delivered to the laboratory

immediately after collection may not meet these criteria. In these cases, the samples shall be considered acceptable if there is evidence that the chilling process has begun, such as arrival on ice.

2) The laboratory shall implement procedures for checking chemical preservation using readily available techniques, such as pH or free chlorine, prior to or during sample preparation or analysis.

With the exception of residual chlorine measurements in aquatic toxicity samples, certain measurements, such a pH, are performed and recorded just prior to analysis.

Field filtration for dissolved metals, Perchlorate and others may also be required. If there is no documentation of field filtration on the Chain of Custody when required, the Project Manager is notified and the client asked. If samples are not field filtered, they are sent to the lab for filtration within 24 or 48 hours depending on the analysis.

b) The results of all checks are recorded on Sample Receipt and, as needed, Sample Anomaly forms.

c) When there is any doubt as to the item's suitability for testing, when the sample does not conform to the description provided, and when the test required is not fully specified, the laboratory makes every attempt to consult the client for further instruction before proceeding. The laboratory establishes whether the sample has received all necessary preparation, or whether sample preparation has yet to be performed. If the sample does not meet the sample receipt acceptance criteria listed in this standard, the laboratory:

1) Retains correspondence and/or records of conversations concerning the final disposition of rejected samples; or

2) Fully documents any decision to commence with the analysis of samples not meeting acceptance criteria.

i. The condition of these samples is, at a minimum, noted on the chain of custody record or transmittal form, and laboratory receipt documents.

ii. The analysis data is/are appropriately "qualified" on the final report.

d) The laboratory utilizes a permanent chronological record such as a logbook or electronic database to document receipt of all sample containers.

1) This sample receipt log records the following:

i. Client/Project Name;

ii. Date and time of laboratory receipt;

iii. Unique laboratory ID code (see ECIQSM Section 11.1); and

iv. Signature or initials of the person making the entries.

2) During the login process, the following information is linked to the log record or included as a part of the log. If such information is recorded/documented elsewhere, that document becomes part of the laboratory's permanent records, easily retrievable upon request, and readily available to individuals who will process the sample. Note: The placement of the laboratory ID number on the sample container is not considered a permanent record.

i. The field ID code that identifies each container is linked to the laboratory ID code in the sample receipt log.

ii. The date and time of sample collection is linked to the sample container and to the date and time of receipt in the laboratory.

iii. The requested analyses (including applicable approved test method numbers) are linked to the laboratory ID code.

iv. Any comments resulting from inspection for sample rejection are linked to the laboratory ID code.

e) All documentation (i.e., memos or transmittal forms) that are conveyed to the laboratory by the sample submitter is retained.

f) A complete chain of custody record form is maintained.

11.5 Storage Conditions

The laboratory has documented procedures and appropriate facilities to avoid deterioration, contamination, and damage to the sample during storage, handling, preparation, and testing; any relevant instructions provided with the item are followed. Where items must be stored or conditioned under specific environmental conditions, these conditions are maintained, monitored, and recorded.

a) Samples are stored according to the conditions specified by preservation protocols:

1) Samples that require thermal preservation are stored under refrigeration at +/-2° of the specified preservation temperature unless method-specified criteria exist. For samples with a specified storage temperature of 4°C, storage at a temperature above the freezing point of water to 6°C is acceptable.

2) Samples are stored away from all standards, reagents, food, and other potentially contaminating sources. Samples are stored in such a manner to prevent cross contamination.

b) Sample fractions, extracts, leachates, and other sample preparation products are stored according to ECIQSM Section 11.4.a above or according to specifications in the test method.

c) When a sample or portion of a sample needs to be held secure (for example, for reasons of record, safety or value, or to enable check calibrations or tests to be performed later), the laboratory has storage and security arrangements that protect the condition and integrity of the secured items or portions concerned.

11.6 Sample Disposal

The laboratory has standard operating procedures for the disposal of samples, digestates, leachates and extracts or other sample preparation products. Refer to SOP T005, Disposal of Laboratory Samples and Wastes.

12.0 RECORDS

The laboratory maintains a record system to suit its particular circumstances and comply with any applicable regulations. The system produces unequivocal, accurate records that document all laboratory activities. The laboratory retains all original observations, calculations and derived data, calibration records and a copy of the test report for a minimum of five years.

There are two levels of sample handling: 1) sample tracking and 2) legal chain of custody protocols that are used for evidentiary or legal purposes. All essential requirements for sample tracking (e.g., chain of custody form) are outlined in ECIQSM Sections 12.1, 12.2 and 12.3. ECI details the Legal/Evidentiary and Internal Chain of Custody procedures in SOP T100, Sample Receipt and Log-In Procedures.

12.1 Record Keeping System and Design

The ECI record keeping system allows historical reconstruction of all laboratory activities that produced the analytical data. The history of the sample is readily understood through the documentation. This includes inter-laboratory transfers of samples and/or extracts.

a) The records include the identity of personnel involved in sampling, sample receipt, preparation, and calibration or testing.

b) All information relating to the laboratory facilities equipment, analytical test methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification, are documented.

c) The record keeping system facilitates the retrieval of all working files and archived records for inspection and verification purposes, e.g., set format for naming electronic files.

d) All changes to records are signed or initialed by responsible staff. The reason for the signature or initials is clearly indicated in the records such as “sampled by,” “prepared by,” or “reviewed by.”

e) All generated data, except those that are generated by automated data collection systems, are recorded directly, promptly, and legibly in permanent ink.

f) Entries in records are not be obliterated by methods such as erasures, overwritten files or markings. All corrections to record-keeping errors are made by one line marked through the error. The individual making the correction signs (or initials) and dates the correction. These criteria also apply to electronically maintained records.

g) Refer to 10.9 for Computer and Electronic Data.

12.2 Records Management and Storage

a) All records (including those pertaining to calibration and test equipment), certificates and reports are safely stored, and held secure and in confidence to the client. NELAP-related records are available to the accrediting authority.

b) All records, including those specified in ECIQSM Section 12.3, are retained for a minimum of five years from generation of the last entry in the records. The laboratory maintains all information necessary for the historical reconstruction of data. Records stored only on electronic media are supported by the hardware and software necessary for their retrieval.

c) Records that are stored or generated by computers or personal computers have hard copy or write-protected backup copies.

d) The laboratory has an established record management system for control of laboratory notebooks, instrument logbooks, standards logbooks, and records for data reduction, validation storage and reporting.

e) Access to archived information is documented with an access log. These records are protected against fire, theft, loss, environmental deterioration, vermin, and in the case of electronic records, electronic or magnetic sources.

f) The laboratory has a plan to ensure that the records are maintained or transferred according to the clients’ instructions (see 4.1.8.e of NELAC) in the event of Laboratory Transfer of Ownership, Going out of Business or Bankruptcy. In all cases, appropriate regulatory and state legal requirements concerning laboratory records will be followed. For detailed policies and procedures for handling of client records and data in these situations, reference QSM Section 6.2.1 and SOP T-002, Document Control.

12.3 Laboratory Sample Tracking

12.3.1 Sample Handling

A record of all procedures to which a sample is subjected while in ECI's possession is maintained. These include but are not limited to all records pertaining to:

a) Sample preservation, including appropriateness of sample container and compliance with holding time requirement;

b) Sample identification, receipt, acceptance or rejection, and log-in;

c) Sample storage and tracking, including shipping receipts, sample transmittal forms (chain of custody form); and

d) Documentation procedures for the receipt and retention of test items, including all provisions necessary to protect the integrity of samples.

12.3.2 Laboratory Support Activities

In addition to documenting all the above-mentioned activities, the following is retained:

a) All original raw data, whether hard copy or electronic, for calibrations, samples and quality control measures, including analysts work sheets and data output records (chromatograms, strip charts, and other instrument response readout records);

b) A written description or reference to the specific test method used, which includes a description of the specific computational steps used to translate parametric observations into a reportable analytical value;

c) Copies of final reports;

d) Archived standard operating procedures;

e) Correspondence relating to laboratory activities for a specific project;

f) All corrective/preventive action reports, audits and audit responses;

g) Proficiency test results and raw data; and,

h) Results of data review, verification, and cross-checking procedures.

12.3.3 Analytical Records

The essential information associated with analyses, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs, include:

a) Laboratory sample ID code;

b) Date of analysis and time of analysis if the method-specified holding time is 72 hours or less, or when time critical steps are included in the analysis, e.g., extractions, and incubations;

c) Instrument identification and instrument operating conditions/parameters (or reference to such data);

d) Analysis type;

e) All manual calculations e.g., manual integrations;

f) Analyst's or operator's initials/signature or chemist ID number;

g) Sample preparation including cleanup, separation protocols, incubation periods or subculture, ID codes, volumes, weights, instrument printouts, meter readings, calculations, reagents;

h) Sample analysis;

i) Standard and reagent origin, receipt, preparation, and use;

j) Calibration criteria, frequency and acceptance criteria;

k) Data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions;

l) Quality control protocols and assessment;

m) Electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries; and,

n) Method performance criteria including expected quality control requirements.

12.3.4 Administrative Records

The following are maintained:

a) Personnel qualifications, experience and training records;

b) Ethics Statements;

c) Records of demonstration of capability for each analyst; and

d) A log of names, initials and signatures for all individuals who are responsible for signing or initialing any laboratory record.

13.0 LABORATORY REPORT FORMAT AND CONTENTS

The results of each test, or series of tests carried out by the laboratory must be reported accurately, clearly, unambiguously and objectively. The results normally reported in a test report and include all the information necessary for the interpretation of the test results and all information required by the method used. Some regulatory reporting requirements or formats, such as monthly operating reports may not require all items listed below, however, ECI will provide all the required information to their client for use in preparing such regulatory reports.

a) Except as discussed in 13.b, each report to an outside client includes at least the following information (those prefaced with “where relevant” are not mandatory):

    1) A title, e.g., "Analytical Report," or "Test Certificate," "Certificate of Results" or "Laboratory Results”;

    2) Name and address of laboratory, and location where the test was carried out if different from the address of the laboratory and phone number with name of contact person for questions;

3) Unique identification of the certificate or report (such as serial number) and of each page, and the total number of pages;

   This requirement may be presented in several ways:

   i. The total number of pages may be listed on the first page of the report as long as the subsequent pages are identified by the unique report identification and consecutive numbers, or

   ii. Each page is identified with the unique report identification, the pages are identified as a number of the total report pages (example: 3 of 10, or 1 of 20).

   Other methods of identifying the pages in the report may be acceptable as long as it is clear to the reader that discrete pages are associated with a specific report, and that the report contains a specified number of pages.

4) Name and address of client, where appropriate and project name if applicable;

5) Description and unambiguous identification of the tested sample including the client identification code;

6) Identification of test results derived from any sample that did not meet NELAC sample acceptance requirements such as improper container, holding time, or temperature;

7) Date of receipt of sample, date and time of sample collection, date(s) of performance test, and time of sample preparation and/or analysis if the required holding time for either activity is less than or equal to 72 hours;

8) Identification of the test method used, or unambiguous description of any nonstandard method used;

9) If the laboratory collected the sample, reference to sampling procedure;

10) Any deviations from (such as failed quality control), additions to or exclusions from the test method (such as environmental conditions), and any nonstandard conditions that may have affected the quality of results, and including the use and definitions of data qualifiers.

11) Measurements, examinations and derived results, supported by tables, graphs, sketches, and photographs as appropriate, and any failures identified; identify whether data are calculated on a dry weight or wet weight basis; identify the reporting units such as µg/l or mg/kg;

12) When required, a statement of the estimated uncertainty of the test results;

13) A signature and title, or an equivalent electronic identification of the person(s) accepting responsibility for the content of the certificate or report (however produced), and date of issue;

14) At the ECI's discretion, a statement to the effect that the results relate only to the items tested or to the sample as received by the laboratory;

15) At the ECI's discretion, a statement that the certificate or report shall not be reproduced except in full, without the written approval of the laboratory;

16) Clear identification of all test data provided by outside sources, such as subcontracted laboratories, clients, etc.; and

17) Clear identification of numerical results with values outside of quantitation limits.

b) Where the certificate or report contains results of tests performed by subcontractors, these results are clearly identified by subcontractor name or applicable accreditation number and the entirety of the subcontract report is included with the final ECI report.

c) After issuance of the report, the laboratory report remains unchanged. Material amendments to a calibration certificate, test report or test certificate after issue may be made only in the form of a further document, or data transfer, including the statement "Supplement to Test Report or Test Certificate, serial number . . . [or as otherwise identified]", or equivalent form of wording. Such amendments meet all the relevant requirements of the NELAC Standard.

d) ECI notifies clients promptly, in writing, of any event such as the identification of defective measuring or test equipment that casts doubt on the validity of results given in any calibration certificate, test report or test certificate or amendment to a report or certificate.

e) The laboratory will, where clients require transmission of test results by telephone, telex, facsimile or other electronic or electromagnetic means, follow documented procedures that ensure that the requirements of this Standard are met and that confidentiality is preserved.

f) ECI will certify that all its NELAC-certified test results reported meet all requirements of NELAC or provide reasons and/or justification if they do not.

14.0 SUBCONTRACTING ANALYTICAL SAMPLES

When ECI subcontracts work whether because of unforeseen circumstances (e.g. workload, need for further expertise or temporary incapacity) or on a continuing basis (e.g. through client direction, contractual arrangement or permanent subcontracting), this work shall be placed with a laboratory accredited under NELAP, or other appropriate certification, for the tests to be performed or with a laboratory that meets applicable statutory and requirements for performing the tests and submitting the results of tests performed. All subcontracted work shall be referenced and so noted in the final ECI analytical report.

Subcontract laboratories will provide or make available, current copies of the following documents prior to ECI submitting samples. This information will be updated annually or on an as needed basis.

a) Laboratory accreditations / certifications

b) Upon request, any Proficiency Testing (PT) or Performance Evaluation (PE) results relevant to the subcontracted samples.

c) Insurance Certificates

d) Quality Assurance Manual

e) Subcontract laboratories will also submit statements affirming that ECI will be notified if any of the following occur.

- There is a change or loss in accreditation for the applicable analysis.
- Most recent PT or PE study results for the applicable analysis are unacceptable *AND* are not able to be addressed via Corrective Action.
- There is a need to subcontract ECI project samples. Prior ECI approval is required in writing for subcontracting samples.

f) The client project requirements will be used to evaluate the subcontract laboratories and to determine their acceptability. Approval by either: the QA Manager, Laboratory Director or Client Services Director (or designee) is required.

g) A master list of approved laboratories will be created and distributed to Sample Control and all Project Managers. All subcontracting must utilize a laboratory from this list.

The procedure for subcontracting samples will follow these guidelines:

a) ECI will advise its client via written, facsimile or e-mail notification of its intention to subcontract any portion of the testing to another party in cases when unforeseen circumstances occur. ECI shall gain approval by the client in writing, facsimile or via e-mail response.

b) ECI may subcontract samples on a continuing basis without written, facsimile or e-mail notification under the following (but not limited to) cases:

- Standing Client direction or instruction
- Contractual specification or requirement
- Project historical precedent

c) A separate Chain of Custody will be created specifically for the subcontracted sample(s). This (or a copy) will be included with the full and complete subcontract report in the final ECI analytical report.

d) ECI shall retain records demonstrating that the above requirements have been met.

e) If the samples to be subcontracted are submitted to ECI under special regulatory, agency or governmental accreditation, Example: Department of Defense / Energy, that have more comprehensive or differing quality criteria, Example: DOD/DOE QSM for Environmental Laboratories Version 5.0 July 2013, then the subcontract laboratory MUST have certification for the subcontracted analysis from the same entity and MUST have undergone similar assessment as the primary laboratory for the subcontracted component. Written authorization from the client or authorizing body must be obtained prior to usage of each subcontract laboratory.

15.0 OUTSIDE SUPPORT SERVICES AND SUPPLIES

ECI does not procure outside services and supplies, other than those referred to in this Manual.

Service providers and vendors are evaluated in accordance with ISO/IEC 17025:2005 or ISO 9001 guidelines prior to use by ECI, reference SOP T019 and T107 for additional information.

16.0 INQUIRIES AND COMPLAINTS

ECISOP-T018 addresses the policies and procedures for the resolution of inquiries and complaints received from clients or other parties about the laboratory's activities. Where an inquiry or complaint, or any other circumstance, raises doubt concerning the laboratory's compliance with the laboratory's policies or procedures, or with the requirements of this manual or otherwise concerning the quality of the laboratory's calibrations or tests, the laboratory shall ensure that those areas of activity and responsibility involved are promptly audited in accordance with NELAC Section 5.3.1. Records of the complaint and subsequent actions are maintained and are available for audits.

17.0 REVIEW OF WORK REQUESTS, CONTRACTS AND TENDERS

ECI has established procedures for the review of work requests contracts and tenders. Projects, proposals and contracts are reviewed for adequately defined requirements and the ability of ECI to meet those requirements. A thorough review of all technical and quality control requirements contained in these requests is performed to ensure a project's success. The appropriateness of requested methods, and the lab's capability to perform them must be established. A review of the laboratory's capability to analyze non-routine analytes is also part of this review process. Additionally, alternate test methods that are capable of meeting the clients' requirements may be proposed by the lab.

All projects, proposals and contracts are reviewed for the client's requirements in terms of compound lists, test methodology requested, detection and reporting levels, and quality control limits. During the review process, the laboratory determines whether it has the necessary physical, personnel and information resources to meet the project requirements, and if the personnel have the expertise needed to perform the required testing. Each proposal is also checked for its impact on the overall capacity of the laboratory. The proposed turnaround time will be checked for feasibility. Electronic or hard copy deliverable requirements are evaluated against the laboratory's ability to produce such documentation.

This review process ensures that the laboratory's test methods are suitable to achieve regulatory and/or client requirements and that the laboratory holds the appropriate certifications to perform the work. In the event that the use of a subcontract laboratory is needed, also confirming that they meet all project requirements and maintain the appropriate certifications for the proposed subcontract analyses. If the laboratory cannot provide all services and therefore intends to use the services of a subcontract laboratory, this will be documented and discussed with the client prior to project or contract approval.

Following the review process, the laboratory informs the client of the results of the review and notes any potential conflict, lack of accreditation, or inability of the lab to complete the work satisfactorily. Any discrepancy between the client's requirements and the capability of the laboratory to meet those requirements is resolved in writing before acceptance of the project or contract. It is necessary that the project requirements or contract be acceptable to both the client and the laboratory prior to the start of the work. The review process is repeated when there are amendments to the original contract by the client.

All contracts, Quality Assurance Project Plans (QAPPs), Sampling and Analysis Plans (SAPs), contract amendments, and documented communications become part of the project record.

Review Personnel

Depending upon the scope of a project or contract, one or more key persons may review and accept work on behalf of the laboratory. For routine projects, a review by the Project Manager (PM) is considered adequate. The PM confirms that the laboratory has the necessary certifications, that it can meet the clients' data quality, reporting and turn-around time requirements.

For new, complex or large projects, the proposed project proposal or contract is given to the Business Development Director for an initial review that encompasses all facets of the operation. The scope of work is then distributed to the following personnel, as needed based on scope of contract, to evaluate all of the project related requirements:

- Laboratory Director
- Operations Director
- Technical Director
- Quality Assurance Director
- Quality Assurance Manager
- Group Leaders

- Project Manager(s)

Appropriate records are maintained for every contract or work request. Copies of the agreed-upon contract will be distributed to key personnel as needed and the signed copies maintained by the Business Development Director and/or Laboratory Director.

Project Kick-off and Status Meetings

For routine project work, project managers ensure that specific technical and QC requirements are effectively evaluated and communicated to laboratory personnel through the use of the LIMS system: special requirements section of the chemist's worksheet.

Prior to work on a new or complex project, project managers or key personnel will hold meetings with operations personnel to discuss schedules and any unique aspects of the project. Items discussed include the project technical profile, turnaround times, holding times, methods, analyte lists, reporting limits, deliverables, sample hazards, and any other special requirements.

Project requirements are given to the laboratory staff during project kick-off meetings or the daily status meetings. Information disseminated during these meetings provides direction to the laboratory staff in order to maximize production, maintain high quality and ensure client satisfaction.

During the project, changes to the scope of work may occur due to client, sampling or regulatory reasons. If these changes impact the laboratory's role in the project (use of a non-standard method or modification of a method to comply with revised requirements) then the changes need to be discussed with and agreed upon with the client prior to continuing with the work. These changes must be documented prior to implementation and communicated to the laboratory staff during a status or project specific meeting. Documentation of the modification is made in the analytical report narrative.

And at all times, records of all pertinent discussions with a client relating to the project or contract are documented and maintained as a part of the project record.

18.0 MANAGEMENT REVIEW, MANAGEMENT OF CHANGE AND CONTINUOUS IMPROVEMENT

18.1 Management Review

A comprehensive Management Review of the entire ECI Quality System will be conducted by the Laboratory Director on an annual basis, no later than the end of the first quarter for the previous year's review. The SOP T-030 may be consulted for detailed guidance. All major stakeholders will be given an opportunity to provide comment or input for the review. These will include:

- Laboratory Director
- Client Services Director
- Operations Director
- Technical Director
- Senior Project Manager
- Other Operational / Project Management personnel as appropriate.
- Clients

The purpose and goal of the Management Review will identify weaknesses, areas requiring more resources or oversight, opportunities for continuous improvement and follow up on previous recommendations.

The final completed review is part of the NELAP laboratory documentation requirements and may be submitted to ECI authorized auditing agencies or clients upon request.

18.2 Management of Change

Whenever a change is made in a controlled environment (not just production) the laboratory is put at risk. However, one needs to constantly make changes to keep pace with business / regulatory requirements. The challenge to the laboratory is to minimize the risk and impact of that change.

An organization must have an operating process in place for which an evaluation has been conducted, and that allows proper lead times and approvals to ensure that the laboratory is unaffected when changes are made. But to successfully implement a change, one also needs to have a comprehensive understanding of the infrastructure that supports the services to determine the overall impact. The Management of Change process will facilitate, as referenced in SOP T030, this evaluation.

The Management of Change process will track and implement the following types of changes:

a) Permanent Change: – A change that is considered long term and durable. Any change which is not categorized as a Temporary Change.

b) Temporary Change: – A change which has a defined lifetime and which will be removed before a defined date (usually no more than six months). All temporary changes must have a specified removal date that is documented on the approved MOC form.

c) Emergency Change: – An emergency change path that allows the change to be implemented and commissioned immediately in order to address an immediate safety, operational, health, environmental, or product quality situations.

The functional categories that will be managed include:

a) Laboratory Facility Acquisition
b) Laboratory Instrument Acquisition
c) Analytical Method Development and Validation
d) Laboratory Operations Process Change
e) Department Relocation
f) Activation of Analytical Method
g) Information Technology (Major Initiatives)
h) New Accreditation or Certification

18.3 Continuous Improvement

In order for ECI to be proactive and a leader in the industry, the entire ECI Quality system is designed to ensure the production of scientifically sound, legally defensible data of known and proven quality. The addition of the Management Review and Management of Change processes enhances ECI's ability to foster continuous improvement.

Continuous improvement is an ongoing effort to improve data integrity, services or processes. These efforts can seek "incremental" improvement over time or "breakthrough" improvement all at once. All staff at ECI participates in continuous improvement, from the Laboratory Director down to the beginning technician, as well as external stakeholders when applicable.

The following procedures / inputs have direct involvement in the continuous improvement process:

a) External Audits (Regulatory and Client Based)
b) Internal Audits
c) Corrective / Preventive Actions
d) Statistical Quality Control (SQC) Monitoring
e) Proficiency Testing Performance
f) Client Feedback – Complaints and Commendations
g) Management Review
h) Management of Change

The Management of Change process will guide and document the major improvements. The Corrective / Preventive Action procedure will enable and record the more incremental changes.

The principal elements are commitment to quality, focused effort, involvement of all employees, willingness to change, and communication.

NELAC APPENDICES

APPENDIX A - REFERENCES

NELAC Standards, Chapters 1-6. Adopted September 8, 2009, Effective July 01, 2010

40 CFR Part 136, Appendix A, paragraphs 8.1.1 and 8.2.

American Association for Laboratory Accreditation April 1996. General Requirements for Accreditation.

"American National Standards Specification and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs (ANSI/ASQC E-4)," 1994.

ASTM E1598-94 Conducting Early Seedling Growth Tests, American Society for Testing and Materials, West Conshocken, PA 1999.

ASTM E11676-97 Conducting a Laboratory Soil Toxicity Test with Lumbricid Earthworm *Eisenia foetida*, American Society for Testing and Materials, West Conshocken, PA 1999.

Catalog of Bacteria, American Type Culture Collection, Rockville, MD.

EPA 2185 - Good Automated Laboratory Practices, 1995 available at www.epa.gov/docs/etsdwe1/irm_galp/

EPA/600/3-89/013 Ecological Assessment of Hazardous Waste Sites, Office of Research and Development, Washington, DC, 1991.

EPA/503/8-91/001 Evaluation of Dredged Material Proposed for Ocean Disposal – Testing Manual. Office of Water, Washington, DC, 1991.

EPA/600/4-90/031 Manual for Evaluation of Laboratories Performing Aquatic Toxicity Tests, Office of Research and Development, Washington, DC, 1991.

EPA/600/3-88/029 Protocol for Short-term Toxicity Screening of Hazardous Wastes, Office of Research and Development, Washington, DC, 1991.

EPA/600/4-90/027F Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 4th Ed., Office of Research and Development, Washington, DC, 1993.

EPA/823/B-98/004 Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. – Inland Testing Manual. Office of Water, Washington, DC, 1994.

EPA/600/R-94/025 Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine Amphipods, Office of Research and Development, Washington, DC, 1994.

EPA/600/R-94/024 Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates, Office of Research and Development, Washington, DC, 1994.

EPA/600/4-91/002 Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 3rd Ed., Office of Research and Development, Washington, DC, 1994.

EPA/600/4-91/003 Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine and Estuarine Organisms, 2nd Ed., Office of Research and Development, Washington, DC, 1994.

"Glossary of Quality Assurance Terms and Acronyms," Quality Assurance Division, Office of Research and Development, USEPA.

"Guidance on the Evaluation of Safe Drinking Water Act Compliance Monitoring Results from Performance Based Methods," September 30, 1994, Second draft.

ISO/IEC 17025: 2005. General requirements for the competence of calibration and testing laboratories.

“Laboratory Biosafety Manual,” World Health Organization, Geneva, 1983.

Manual for the Certification of Laboratories Analyzing Drinking Water, Revision 4, EPA 815-B-97-001.

Performance Based Measurement System, EPA EMMC Method Panel, PBMS Workgroup, 1996.

APPENDIX B - GLOSSARY

The following definitions are used in the text of Quality Systems. In writing this document, the following hierarchy of definition references was used: ISO 8402, ANSI/ASQC E-4, EPA's Quality Assurance Division Glossary of Terms, and finally definitions developed by NELAC. The source of each definition, unless otherwise identified, is the Quality Systems Committee.

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)

Accreditation: The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (NELAC)

Accrediting Authority: The Territorial, State, or Federal agency having responsibility and accountability for environmental laboratory accreditation and which grants accreditation. (NELAC) [1.5.2.3]

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)

Analysis Duplicate: The second measurement of the target analyte(s) performed on a single sample or sample preparation.

Analyst: The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality. (NELAC)

Analytical Reagent (AR) Grade: Designation for the high purity of certain chemical reagents and solvents given by the American Chemical Society. (Quality Systems)

Assessment: The evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of NELAC). (NELAC)

Audit: A systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (EPA-QAD)

Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)

Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)

Blind Sample: A sub-sample for analysis with a composition known to the submitter. The analyst/ laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (NELAC)

Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)

Calibration Curve: The graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (NELAC)

Calibration Method: A defined technical procedure for performing a calibration. (NELAC)

Calibration Standard: A substance or reference material used to calibrate an instrument. (QAMS)

Certified Reference Material (CRM): A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30 - 2.2)

Chain of Custody Form: A record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; collector; time of collection; preservation; and requested analyses. (NELAC)

Compromised Samples: Those samples which are improperly sampled, insufficiently documented (chain of custody and other sample records and/or labels), improperly preserved, collected in improper containers, or exceeding holding times when delivered to a laboratory. Under normal conditions compromised samples are not analyzed. If emergency situations require analysis, the results must be appropriately qualified. (NELAC)

Confirmation: Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to:

- Second column confirmation;
- Alternate wavelength;
- Derivatization;
- Mass spectral interpretation;
- Alternative detectors; or
- Additional cleanup procedures. (NELAC)

Conformance: An affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ ASQC E4-1994)

Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)

Data Audit: A qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria). (NELAC)

Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form. (EPA-QAD)

Deficiency: An unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC)

Demonstration of Capability: A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)

Desorption Efficiency: The mass of target analyte recovered from sampling media, usually a sorbent tube, divided by the mass of target analyte spiked on to the sampling media expressed as a percentage. Sample target analyte masses are usually adjusted for the desorption efficiency. (NELAC)

Detection Limit: The lowest concentration or amount of the target analyte that can be identified, measured, and reported with confidence that the analyte concentration is not a false positive value. See Method Detection Limit. (NELAC)

Document Control: The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC)

Duplicate Analyses: The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA- QAD)

Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised. (40 CFR Part 136)

Inspection: An activity such as measuring, examining, testing, or gauging one or more characteristics of an entity and comparing the results with specified requirements in order to establish whether conformance is achieved for each characteristic. (ANSI/ ASQC E4-1994)

Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method. (NELAC)

Instrument Blank: A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD)

Laboratory: A body that calibrates and/or tests. (ISO 25)

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC)

Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (NELAC)

Limit of Detection (LOD): Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. (NELAC)

Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias. (NELAC)

Manager (however named): The individual designated as being responsible for the overall operation, all personnel, and the physical plant of the environmental laboratory. A supervisor may report to the manager. In some cases, the supervisor and the manager may be the same individual. (NELAC)

Matrix: The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

- Aqueous: Any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts.
- Drinking Water: Any aqueous sample that has been designated a potable or potential potable water source.
- Saline/Estuarine: Any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.
- Non-aqueous Liquid: Any organic liquid with <15% settleable solids.
- Biological Tissue: Any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.
- Solids: Includes soils, sediments, sludges and other matrices with >15% settleable solids.
- Chemical Waste: A product or by-product of an industrial process that results in a matrix not previously defined.
- Air: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter or other device. (NELAC)

Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte. (QAMS)

May: Denotes permitted action, but not required action. (NELAC)

Media: Material that supports the growth of a microbiological culture.

Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. (NELAC)

Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (40 CFR Part 136 Appendix B)

Must: Denotes a requirement that must be met. (Random House College Dictionary)

National Accreditation Database: The publicly accessible database listing the accreditation status of all laboratories participating in NELAP. (NELAC)

National Environmental Laboratory Accreditation Conference (NELAC): A voluntary organization of State and Federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories. A subset of NELAP. (NELAC)

National Environmental Laboratory Accreditation Program (NELAP): The overall National Environmental Laboratory Accreditation Program of which NELAC is a part. (NELAC)

Negative Control: Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results. (NELAC)

Objective Evidence: Any documented statement of fact, other information, or record, either quantitative or qualitative, pertaining to the quality of an item or activity, based on observations, measures, or tests that can be verified. (ASQC)
Performance Audit: The routine comparison of independently obtained qualitative and quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory. (NELAC)

Performance Based Measurement System (PBMS): A set of processes wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner. (NELAC)

Positive Control: Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects. (NELAC)

Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)

Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample. (NELAC)

Proficiency Testing: A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (NELAC) [2.1]

Proficiency Testing Program: The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (NELAC)

Proficiency Test Sample (PT): A sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (QAMS)

Protocol: A detailed written procedure for field and/or laboratory operation (e.g., sampling, and analysis) which must be strictly followed. (EPA- QAD)

Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method. (NELAC)

Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)

Quality Assurance (Project) Plan (QAPP): A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved. (EPA-QAD)

Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. (QAMS)

Quality Control Sample: An uncontaminated sample matrix with known amounts of analytes from a source independent from the calibration standards. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (EPA-QAD)

Quality Manual: A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users. (NELAC)

Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC. (ANSI/ ASQC E-41994)

Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence. (NELAC)

Range: The difference between the minimum and the maximum of a set of values. (EPA-QAD)

Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted. (EPA-QAD)

Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (QAMS)

Record Retention: The systematic collection, indexing and storing of documented information under secure conditions. (EPA-QAD)

Reference Material: A material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (ISO Guide 30- 2.1)

Reference Method: A method of known and documented accuracy and precision issued by an organization recognized as competent to do so. (NELAC)

Reference Standard: A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived. (VIM-6.08)

Reference Toxicant: The toxicant used in performing toxicity tests to indicate the sensitivity of a test organism and to demonstrate the laboratory's ability to perform the test correctly and obtain consistent results (see Chapter 5, Appendix D, Section 2.1.f). (NELAC)

Replicate Analyses: The measurements of the variable of interest performed identically on two or more sub-samples of the same sample within a short time interval. (NELAC)

Requirement: Denotes a mandatory specification; often designated by the term "shall". (NELAC)

Sampling Media: Material used to collect and concentrate the target analytes(s) during air sampling such as solid sorbents, filters, or impinger solutions.

Selectivity: (Analytical chemistry) The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. (EPA-QAD)

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (NELAC)

Shall: Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. This does not prohibit the use of alternative approaches or methods for implementing the specification so long as the requirement is fulfilled. (ANSI)

Should: Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)

Spike: A known mass of target analyte added to a blank sample or sub-sample; used to determine recovery efficiency or for other quality control purposes. (NELAC)

Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies. (ASQC)

Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks. (QAMS)

Standardized Reference Material (SRM): A certified reference material produced by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. (EPA-QAD)

Supervisor (however named): The individual(s) designated as being responsible for a particular area or category of scientific analysis. This responsibility includes direct day-to-day supervision of technical employees, supply and instrument adequacy and upkeep, quality assurance/quality control duties and ascertaining that technical employees have the required balance of education, training and experience to perform the required analyses. (NELAC)

Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes. (QAMS)

Systems Audit (also Technical Systems Audit): A thorough, systematic, qualitative on-site assessment of the facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a total measurement system. (EPA-QAD)

Technical Director: Individual(s) who has overall responsibility for the technical operation of the environmental testing laboratory. (NELAC)

Test: A technical operation that consists of the determination of one or more characteristics or performance of a given product, material, equipment, organism, physical phenomenon, process or service according to a specified procedure. The result of a test is normally recorded in a document sometimes called a test report or a test certificate. (ISO/IEC Guide 2-12.1, amended)

Test Method: An adoption of a scientific technique for a specific measurement problem, as documented in a laboratory SOP. (NELAC)

Testing Laboratory: Laboratory that performs tests. (ISO/ IEC Guide 2 - 12.4)

Test Sensitivity/Power: The minimum significant difference (MSD) between the control and test concentration that is statistically significant. It is dependent on the number of replicates per concentration, the selected significance level, and the type of statistical analysis (see Chapter 5, Appendix D, Section 2.4.a). (NELAC)

Tolerance Chart: A chart in which the plotted quality control data is assessed via a tolerance level (e.g. +/- 10% of a mean) based on the precision level judged acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. +/- 3 sigma) (applies to radiobioassay laboratories). (ANSI)

Traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (VIM - 6.12)

Validation: The process of substantiating specified performance criteria. (EPA- QAD)

Verification: Confirmation by examination and provision of evidence that specified requirements have been met. (NELAC)

NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment.

The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.

Work Cell: A well-defined group of analysts that together perform the method analysis. The members of the group and their specific functions within the work cell must be fully documented. (NELAC)

Sources:

American Society for Quality Control (ASQC), Definitions of Environmental Quality Assurance Terms, 1996

American National Standards Institute (ANSI), Style Manual for Preparation of Proposed American National Standards, Eighth Edition, March 1991

ANSI/ASQC E4, 1994

ANSI N42.23- 1995, Measurement and Associated Instrument Quality Assurance for Radiobioassay Laboratories

International Standards Organization (ISO) Guides 2, 30, 8402

International Vocabulary of Basic and General Terms in Metrology (VIM): 1984. Issued by BIPM, IEC, ISO and OIML

National Institute of Standards and Technology (NIST)

National Environmental Laboratory Accreditation Conference (NELAC), July 1998 Standards

Random House College Dictionary

U.S. EPA Quality Assurance Management Section (QAMS), Glossary of Terms of Quality Assurance Terms, 8/31/92 and 12/6/95

U.S. EPA Quality Assurance Division (QAD)

40 CFR, Part 136

Webster's New World Dictionary of the American Language

APPENDIX C - DEMONSTRATION OF CAPABILITY

C.1 PROCEDURE FOR DEMONSTRATION OF CAPABILITY

A demonstration of capability (DOC) must be made prior to using any test method, and at any time there is a change in instrument type, personnel or test method. (See NELAC 10.2.1.)

Note: Where tests are performed by specialized "work cells" (a well-defined group of analysts that together perform the method analysis), the work cell as a unit meets the above criteria and this demonstration is fully documented.

In general, this demonstration does not test the performance of the method in real world samples, but in the applicable and available clean matrix (a sample of a matrix in which no target analytes or interferences are present at concentrations that impact the results of a specific test method), e.g., water, solids and air. However, before any results are reported using this method, actual sample spike results may be used to meet this standard, i.e., at least four consecutive matrix spikes within the last twelve months. In addition, for analytes that do not lend themselves to spiking, e.g., TSS, the demonstration of capability may be performed using quality control samples.

All demonstrations shall be documented through the use of the form in this appendix.

The following steps, which are adapted from the EPA test methods published in 40 CFR Part 136, Appendix A, are performed if required by mandatory test method or regulation. Note: For analytes for which spiking is not an option and for which quality control samples are not readily available, the 40 CFR approach is one way to perform this demonstration. The laboratory documents that other approaches to DOC are adequate, and this is documented in the laboratory's Quality Manual.

a) A quality control sample is obtained from an outside source. If not available, the QC sample may be prepared by the laboratory using stock standards that are prepared independently from those used in instrument calibration.

b) The analyte(s) is diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified, or if unspecified, to a concentration approximately 10 times the method-stated or laboratory-calculated method detection limit.

c) At least four aliquots are prepared and analyzed according to the test method either concurrently or over a period of days.

d) Using all of the results, the mean recovery ($\overline{X}$) is calculated in the appropriate reporting units (such as µg/L) and the standard deviations of the population sample (n-1) (in the same units) for each parameter of interest. When it is not possible to determine mean and standard deviations, such as for presence/absence and logarithmic values, the laboratory will assess performance against established and documented criteria.

e) Compare the information from (d) above to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory-generated acceptance criteria (if there are no established mandatory criteria). If all parameters meet the acceptance criteria, the analysis of actual samples may begin. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.

f) When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must proceed according to 1) or 2) below.

1) Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with c) above.

2) Beginning with c) above, repeat the test for all parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with c).

C.2 CERTIFICATION STATEMENT

The following certification statement shall be used to document the completion of each demonstration of capability. A copy of the certification statement shall be retained in the personnel records of each affected employee (see ECIQSM Section 6.3 and 12.3.4.b.).

Demonstration of Capability
Certification Statement

Date: Page __of __
Laboratory Name:
Laboratory Address:
Analyst(s) Name(s):

Matrix: _____
Examples: laboratory pure water, soil, air, solid, biological tissue)

Method number, SOP#, Rev #, and Analyte, or Class of Analytes or Measured Parameters:
_____ (examples: barium by 200.7, trace metals by 6010, benzene by 8021, etc.)

We, the undersigned, CERTIFY that:

1. The analysts identified above, using the cited test method(s), which is in use at this facility for the analyses of samples under the National Environmental Laboratory Accreditation Program, have met the Demonstration of Capability.

2. The test method(s) was performed by the analyst(s) identified on this certification.

3. A copy of the test method(s) and the laboratory-specific SOPs are available for all personnel on-site.

4. The data associated with the demonstration capability are true, accurate, complete and self-explanatory (1).

5. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized assessors.

_____	_____	_____
Technical Director's Name and Title	Signature	Date
_____	_____	_____
Quality Assurance Officer's Name	Signature	Date

This certification form must be completed each time a demonstration of capability study is completed.

(1) True: Consistent with supporting data.
Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.
Complete: Includes the results of all supporting performance testing.
Self-explanatory: Data properly labeled and stored so that the results are clear and require no additional explanation.

(Note: Form may be modified so long as the essential items are included in the revised form)

APPENDIX D - ESSENTIAL QUALITY CONTROL REQUIREMENTS

The quality control protocols specified by the laboratory's method manual (10.1.2) shall be followed. The laboratory shall ensure that the essential standards outlined in Appendix D are incorporated into their method manuals.

All quality control measures shall be assessed and evaluated on an ongoing basis and quality control acceptance criteria shall be used to determine the validity of the data. The laboratory shall have procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exists.

The requirements from the body of Chapter 5, e.g., Section 5.4, apply to all types of testing. The specific manner in which they are implemented is detailed in each of the sections of this Appendix, i.e., chemical testing.

The Standard Operating Procedure (SOP) T020 "Internal Quality Control Checks" and the specific analytical method SOPs have a more detailed outline of the quality control procedures.

D.1 CHEMICAL TESTING

D.1.1 Positive and Negative Controls

a) Negative Controls

1) Method Blanks - Shall be performed at a frequency of one per preparation batch of samples per matrix type. The results of this analysis shall be one of the QC measures to be used to assess the batch. The source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem if

i) the blank contamination exceeds a concentration greater than 1/10 of the measured concentration of any sample in the associated sample batch or

ii) the blank contamination exceeds the concentration present in the samples and is greater than 1/10 of the specified regulatory limit.

Any sample associated with the contaminated blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

b) Positive Controls

1) Laboratory Control Sample (LCS) - (QC Check Samples) Shall be analyzed at a minimum of 1 per preparation batch of 20 or less samples per matrix type, except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The results of these samples shall be used to assess the batch. NOTE: The matrix spike (see 2 below) may be used in place of this control as long as the acceptance criteria are as stringent as for the LCS.

a. The NELAC requirements (2009 Standard, Section 1.7.4.2 b) allow the usage of LCS Marginal Exceedance control limits for those analyses with multiple reporting analytes.

b. The NELAC standards state that if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. ME is defined as being beyond the LCS control limit but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

c. The number of allowable marginal exceedance is based on the number of analytes in the LCS. If there is any analyte that exceed the LCS control limits, it does not necessary mean the LCS fails. The NELAC standard states if the number of analytes fails LCS control limits but is within the ME limits, it is acceptable.

2) Matrix Spikes (MS) - Shall be performed at a frequency of one out of every 20 samples per matrix type prepared over time, except for analytes for which spiking solutions are not available such as, total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The selected sample(s) shall be rotated among client samples so that various matrix problems may be noted and/or addressed. Poor performance in a matrix spike may indicate a problem with the sample composition and shall be reported to the client whose sample was used for the spike.

3) Surrogates - Surrogate compounds must be added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with the sample composition and shall be reported to the client whose sample produced the poor recovery.

4) If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample and Matrix Spike. However, in cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene, and PCBs in Method 608), the test method has an extremely long list of components or components that are incompatible, a representative number (minimum of 10%) of the listed components may be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit-specified analytes, and other client-requested components. However, the laboratory shall ensure that all reported components are used in the spike mixture within a two-year time period.

D.1.2 Analytical Variability/Reproducibility

Matrix Spike Duplicates (MSDs) or Laboratory Duplicates - Shall be analyzed at a minimum of 1 in 20 samples per matrix type per sample extraction or preparation method. The laboratory shall document its procedure to select the use of appropriate type of duplicate. The selected sample(s) shall be rotated among client samples so that various matrix problems may be noted and/or addressed. Poor performance in the duplicates may indicate a problem with the sample composition and shall be reported to the client whose sample was used for the duplicate.

D.1.3 Method Evaluation

In order to ensure the accuracy of the reported result, the following procedures shall be in place:

a) Demonstration of Analytical Capability - (Section 10.5) shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

b) Calibration - Calibration protocols specified in Section 9.4 shall be followed.

c) Proficiency Test Samples - The results of such analyses (4.2.j or 5.3.4) shall be used by the laboratory to evaluate the ability of the laboratory to produce accurate data.

D.1.4 Analytical Measurement Uncertainty Estimation

Uncertainty is “a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand” (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1).

Uncertainty is not error. Error is a single value, the difference between the true result and the measured result. For environmental samples, the true result is never known. The measurement is the sum of the unknown true value and the unknown error.

Unknown error is a combination of systematic error, or bias, and random error. Bias varies predictably, constantly, and independently from the number of measurements. Random error is unpredictable, assumed to have a Gaussian distribution, and be reducible by increasing the total number of measurements.

Knowledge of the uncertainty of a measurement provides additional confidence in the validity of a result as its value accounts for all the factors which could possibly affect the result. Certain test methods will specify limits to the values of sources of uncertainty of measurement (EPA 500 series methods, etc.) and will specify the form of presentation of calculated results.

When the method makes these stipulations, there is no need to provide a mechanism for calculating the uncertainty. Where this information is not provided within a method or other regulatory device, the uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte because LCS recoveries incorporate all of the laboratory-related variables associated with a given test over time. It is recognized that other approaches exist; however, ECI's standard for estimating analytical data uncertainty uses this approach.

D.1.4.1 Using the Laboratory Control Sample (LCS) to Estimating Analytical Uncertainty

a) The estimated measurement uncertainty can be expressed as a range (±) around the reported analytical results at a specified confidence level. For methods that use statistically-derived LCS control limits based on historical LCS recovery data to assess the performance of the measurement system, these limits are considered an estimate of the minimum laboratory contribution to measurement uncertainty at a 99% confidence interval, The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

- Uncertainty values may be reported for specific projects upon request. In absence of alternate client-specified approaches or confidence levels,

  ECI will use the following procedure:

  > To calculate the uncertainty value of a reported analytical result, the lower uncertainty range value is calculated by subtracting the product of the result and the lower LCS percent recovery from the result; and the upper uncertainty value result is calculated by adding the product of the result and the upper LCS percent recovery.
  >
  > These calculated values represent approximately a 99% confidence level. In other words, approximated 99% of the measured values for the analyte will fall within this calculated range.

- Example: If the reported result is 1.0 mg/l, and the LCS percent recovery range is 75 to 125%. The uncertainty range would be 0.75 to 1.25 mg/l, which could also be written as 1.0 +/- 0.25 mg/l.

- The Laboratory Quality and Accreditation Office has made available to the public both a spreadsheet that calculates analytical measurement uncertainty and an SOP describing how to use it. This SOP applies to test methods that are within the scope of ISO/IEC 17025-1999 Standard: General Requirements for the Competence of Testing and Calibration Laboratories and it is based on the general rules outlined in Guide to the Expression of Uncertainty in Measurement (GUM).

The spreadsheet provides a QC-based nested approach for estimating measurement uncertainty using laboratory generated calibration and QC spike results. This spreadsheet has been authorized to be used on DOD/DOE projects, if requested.

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D.1.4.2 Additional Components to Estimating Analytical Uncertainty

When estimating analytical measurement uncertainty, all significant components of uncertainty must be identified and quantified. Components that affect analytical measurement uncertainty include sampling, handling, transport, storage, preparation and testing. A typical environmental laboratory will have the greatest contribution to uncertainty in the storage, preparation and testing portion of the analytical train, hence the estimation can be limited to those three areas, assuming all other factors are within recommended guidelines for sample size, container type, preservation (chemical, temperature, temporal) and handling/transport. If the latter are *NOT* within guidelines then these additional estimations of variability must be accounted for, and may supersede the laboratory contribution to uncertainty.

Definitive references and procedural manuals for calculating Analytical Measurement Uncertainty are listed below. Note that there are different theories on the "best" way to estimate uncertainty, it is up to the end user to determine that which best meets their project needs.

a) "Environmental Analytical Measurement Uncertainty Estimation – Nested Hierarchical Approach", William Ingersoll, Defense Technical Information Center # ADA396946, 2001

b) "Quantifying Uncertainty in Analytical Measurement", EuraChem / CITAC Guide CG 4, Second Edition, QUAM 2000.1

c) "Quantifying Measurement Uncertainty in Analytical Chemistry – A Simplified Practical Approach", Thomas W. Vetter, National Institute of Standards and Technology

d) ISO Guide to the Expression of Uncertainty in Measurement (GUM), 1993

e) "Estimation of Analytical Measurement Uncertainty - Laboratory Quality and Accreditation Office Uncertainty Calculator Standard Operating Procedure. Downloaded from http://www.denix.osd.mil/edqw/upload/UNCERTAINTY-SOP.PDF , 2013

f) QC-based Nested Approach for Estimating Measurement Uncertainty Spreadsheet, Microsoft Excel Spreadsheet, Ingersoll, William Stephen, 2002

The process in general involves the following steps:

1. Specify the Measurand – Write down a clear statement of what is being measured, including the relationship between the measurand and the input quantities, i.e., measured quantities, constants, calibration standard values, etc.

2. Identify uncertainty sources – This will include sources that contribute to the uncertainty on the parameters in the relationships identified in step 1, but may include other sources and must include sources arising from chemical assumptions.

3. Quantify uncertainty components – Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified. It is often possible to estimate or determine a single contribution to uncertainty from the aggregate of multiple sources.

4. Calculate combined uncertainty – The information obtained in step 3 will consist of a number of quantified contributions to overall uncertainty, whether associated with individual sources or with the combined effects of several sources.

The process outlined above relates to the measurement of uncertainty for the preparative / analytical laboratory procedure. However, there are uncertainty contributions from other factors outside the preparative / analytical procedure. These can be controlled to a great extent by specifying uniform and standardized training or conditions.

Examples:

Human Factors

a) All personnel at ECI undergo documented training in the method and / or instrument used. Minimum levels of education or experience are required.

b) Initial and continuing Demonstrations of Capability (DOC) must be performed and documented prior to and in continuance of analytical work related to their areas of responsibilities.

c) Blind Proficiency Testing samples are analyzed twice a year to gauge each department, matrix and method.

d) Data Integrity and Ethics Training are provided to new employees and on an annual basis to all employees.

Accommodation and Environmental Conditions

a) ECI has standardized operating procedures for transport, storage and tracking of samples, extracts and digests throughout the laboratory. All incoming orders are logged into a Laboratory Information System that assigns a specific identifier code to each work order, sample container and analytical result.

b) The sample control areas are secured with restricted access using card key portals. Internal chain of custody is available if the project requires.
c) The laboratory has over 35,000 sq ft of laboratory space with temperature controlled and air positive or negative environmental controls.

d) Regular safety inspections are performed to identify potentially hazardous conditions and to ensure general cleanliness.

Environmental Test Methods and Method Validation

a) All methods in use have Standard Operating Procedures (SOPs) based upon published methods from the EPA, ASTM, Standard Methods or other established body. These are controlled documents assigned to each department. An annual review is performed.

b) Each method has internal and external quality control criteria for preparative efficiency, instrument performance, calibration, continuing method performance and possible matrix effects as appropriate.

c) Ongoing Proficiency Testing program.

Equipment and Instrumentation

a) Each instrument in use has performance parameters that must be evaluated to specific standards based on the established method prior to any analytical use.

b) Routine and preventative maintenance is performed to maintain optimum operational performance.

c) Complex instrument systems are covered under manufacturer service contracts as appropriate.

Measurement Traceability

a) Every reagent used must meet the indicated purity and fitness for usage as referenced in the method SOPs.

b) All calibration standards are certified by the manufacturer to meet or exceed purity levels as recorded in the accompanying Certificate of Traceability to NIST or other standards verification.

c) Each reagent, standard or working standard is recorded, assigned a tracking identifier. This is referenced in the analytical log book as needed to assure traceability to the original source.

d) All Balances, Dispensers, Pipettors, Refrigerators, Freezers and Thermometers are checked on a daily or other routine basis to specified tolerances.

D.1.5 Detection Limits

The laboratory shall utilize a test method that provides a detection limit that is appropriate and relevant for the intended use of the data. Detection limits shall be determined by the protocol in the mandated test method or applicable regulation, e.g., Method Detection Limit (MDL). If the protocol for determining detection limits is not specified, the selection of the procedure must reflect instrument limitations and the intended application of the test method. Refer to SOP T006, Determination of Detection Limits.

a) A detection limit study is not required for any component for which spiking solutions or quality control samples are not available such as temperature.

b) The detection limit shall be initially determined for the compounds of interest in each test method in a matrix in which there are not target analytes nor interferences at a concentration that would impact the results or the detection limit must be determined in the matrix of interest (see definition of matrix).

c) Detection limits must be determined each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis.

d) All samples processing steps of the analytical method shall be included in the determination of the detection limit.

e) All procedures used must be documented. Documentation must include the matrix type. All supporting data must be retained.

f) The laboratory must have established procedures to relate detection limits with quantitation limits.

g) The test method's quantitation limits must be established and must be above the detection limits.

D.1.6 Data Reduction

The procedures for data reduction, such as use of linear regression, shall be documented.

D.1.7 Quality of Standards and Reagents

a) The source of standards shall comply with 9.3.

b) Reagent Quality, Water Quality and Checks:

1) Reagents - In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used. The labels on the container should be checked to verify that the purity of the reagents meets the requirements of the particular test method. Such information shall be documented.

2) Water - The quality of water sources shall be monitored and documented and shall meet method specified requirements.

3) The laboratory will verify the concentration of titrants in accordance with written laboratory procedures.

D.1.8 Selectivity

a) Absolute retention time and relative retention time aid in the identification of components in chromatographic analyses and to evaluate the effectiveness of a column to separate constituents. The laboratory shall develop and document acceptance criteria for retention time windows.

b) A confirmation shall be performed to verify the compound identification when positive results are detected on a sample from a location that has not been previously tested by the laboratory. Such confirmations shall be performed on organic tests such as pesticides, herbicides, or acid extractable or when recommended by the analytical test method except when the analysis involves the use of a mass spectrometer. Confirmation is required unless stipulated in writing by the client. All confirmation shall be documented.

c) The laboratory shall document acceptance criteria for mass spectral tuning.

D.1.9 Constant and Consistent Test Conditions

a) The laboratory shall assure that the test instruments consistently operate within the specifications required of the application for which the equipment is used.

b) Glassware Cleaning - Glassware shall be cleaned to meet the sensitivity of the test method.

Any cleaning and storage procedures that are not specified by the test method shall be documented in laboratory records and SOPs.

D.1.10 Method Validation – Modified Procedures, Non-Standard Methods, Additional Analytes

Often times, modifications to published methods are promulgated to allow the laboratory flexibility, increased productivity and, in some cases, it allows for better hazardous waste management, all while maintaining the quality of the data generated. But, this cannot be done without following standard method validation procedures to guarantee that the results achieved from the modified version are equal to or greater than the actual published or routinely accepted method.

Validation procedures are done to make sure that the sensitivity and selectivity of the process is appropriate for the method or analytes chosen. Interference checks are performed to show that the changes or additions will not contribute interferences to previous analytes or on-going processes. Accuracy and precision requirements are established, or previously defined, and used to demonstrate the capability of an analyst to perform the method, initially and on-going.

In the event that a non-standard method (significantly modified or newly-developed) is needed to meet client requirements, the method specifications and how they impact the project requirements must be relayed to the client for approval prior to beginning work on project samples. The client must understand the limits of the method, why it was developed and when it will be used on their project samples, and they must agree to its use.

Any significantly modified or newly-developed method (including the addition of analytes to established procedures) must be fully defined in a Standard Operating Procedure. The validation must be performed by qualified personnel, using appropriate reagents, standards and equipment/instrumentation and that process must be documented. The following items must be performed (as applicable to the method) and the completed documentation with all raw data provided to the Operations Manager and QA Manager for review prior to granting approval for use. A new method cannot be put into production without Operations and QA approval. For situations where NELAP approval is being sought, the method cannot be used for client samples until the certification has been received from the State, unless approval is given by the client.

D.1.10.1 Significant Modification / New Method / Additional Analyte Documentation:

Prior to the acceptance of client samples for analysis, the following documentation, as applicable to the type of modification or method status, must be provided to both Operations and QA for review and approval.

1. Approved Standard Operating Procedure for Analytical or Preparation Processes. Include all related raw data for the SOP revision with the draft version.

    a) Modification of existing method: - Revised SOP with modifications clearly spelled out:

    b) New Method: - New SOP in NELAC format – QA will assign SOP number

    c) Additional Analytes: - Revised SOP with modifications clearly spelled out:

2. Method Detection Limit (MDL) Study: Compliant with 40CFR, Part 136.

    a) Include summary form and all raw data for the review

3. MDL Verification Standard spiked at 1-4x the MDL, or the level specified by the specific program or contract. Example: 1-2x the MDL, reference specific program requirements.

    b) Recovery within 30 -150%, or a minimum response distinguishable from the established instrument noise level.

4. Reporting Limit Verification (when an MDL verification is not performed)

    a) For analytical methods, reprocess the low calibration standard as percent recovery – recovery between 50% and 150% is acceptable.

    b) For extraction methods, or where required by project or program, spike a blank matrix at the reporting limit and process through all steps of the procedure. Note the spike level and percent recoveries. Method defined control limits are used for recovery evaluation, or default recoveries between 40% and 160% if method defined limits are not available.

5. Tuning Check (as applicable to the method)

6. Degradation Check (as applicable to the method)

7. A Valid Initial Calibration and Verification

    a) Minimum of 5 sequential points, unless otherwise stated in the method or in-house SOP.

    b) Low calibration standard at or below the Reporting/Quantitation Limit.

    c) Initial Calibration Verification Standard

8. Retention Time Window Study

9. Second Column Confirmation for all analytes (as applicable to the method)

10. Inter-element Correction (as applicable to the method)

11. Linear Range Study (as applicable to the method)

12. GCMS Spectral Profile(s) (as applicable to the method)

13. Interference Check – Method Blank

    a) Analysis of a blank matrix that has gone through all related steps, preparation and /or analysis, as applicable.

14. Acceptable PT Sample required for all new analytes where NELAP accreditation is being sought.

    a) At least one PT sample (preferably two) required for all new methods

    b) Where a PT sample is not available, or accreditation is not needed, accuracy can be measured through the use of a second source standard.

15. For California ELAP or State NELAP, process a real world sample for MS and MSD. The sample does not have to contain any target analytes but recoveries for surrogates, internal standards and spikes must be within lab or method defined criteria.

    a) Use Tap Water for drinking water only methods, tap or other clean water source for ground, surface, etc. methods

    b) Local Soil sample for SW-846 methods (if applying for soil or soil/water)

16. Initial Demonstration of Capability (IDOC) per analyst

    a) 4 LCS for each matrix, spiked with all associated new analytes – most acceptance criteria are in the methods, if none, use an initial recovery range of 40-160% and an RPD of 30%.

    b) Non-Standard methods – Follow the procedure in the 2003 NELAC Standards, Chapter 5 appendix C.3.3 (b).

17. Certification / Approval from Regulatory Agency where available.

APPENDIX E – LIST OF ACCREDITED METHODS

- **Arizona Department of Health Services – Laboratory ID AZ0781**

  a) View at: http://www.eurofinsus.com/media/161879/arizona-cert_scope_031216.pdf

- **California SWRCB ELAP – Laboratory ID 2944**

  a) View at: http://www.eurofinsus.com/media/162063/ca-elap_calscience.pdf

- **Guam Environmental Protection Agency – Laboratory ID E971101**

  a) View at: http://www.eurofinsus.com/media/161875/guam-cert_foas_103115.pdf

- **Hawaii Department of Health – Laboratory ID (None)**

  a) View at: http://eurofinsus.com/media/161878/hawaii-cert_093015.pdf

- **Kansas Department of Health & Environment – Laboratory ID E-10409**

  a) View at: http://www.eurofinsus.com/media/16055/kansas1.pdf
  b) View at: http://www.eurofinsus.com/media/16056/kansas2.pdf

- **Nevada Department of Conservation and Natural Resources – Laboratory ID CA001112013-1**

  a) View at: http://www.eurofinsus.com/media/162008/nevada-cert-2015.pdf

- **Oklahoma Department of Environmental Quality – Laboratory ID 1311**

  a) View at: http://www.eurofinsus.com/media/161882/oklahoma-cert_083115.pdf

- **Oregon Environmental Laboratory Accreditation Program (NELAP Primary) – Laboratory ID CA300001**

  a) View at: http://www.eurofinsus.com/media/161877/oregon-state-primary-nelap-cert_012916.pdf

- **Texas Commission of Environmental Quality – Laboratory ID T104704499-14-4**

  a) View at: http://www.eurofinsus.com/media/161881/texas-cert_073115.pdf

- **United States Department of Agriculture Certificate No. P330-10-00403, Permit to Receive Soil**

  a) View at: http://eurofinsus.com/media/16042/usda_soil_permit.pdf

- **United States Department of Agriculture – Authorization to Receive Plant Material**

  b) View at: http://www.eurofinsus.com/media/162229/usda-plant-import-authorization_050615.pdf

- **United States Army Corp of Engineers – Approval (EPA 8270 SIM – PCB Congeners)**

  a) View at: http://www.eurofinsus.com/media/16039/dmmo_epa8270sim.pdf

- **United States Department of Defense / Energy ANAB/ACLASS ELAP Certificate ADE-1864 and Fields of Accreditation**

  a) View at: http://www.eurofinsus.com/media/16049/dod_elap.pdf

- **United States Department of the Interior – Approval**

  b) View at: http://www.eurofinsus.com/media/16067/usbor.pdf

- **Utah Department of Health – Laboratory ID CA00111**

  a) View at: http://www.eurofinsus.com/media/161880/utah-cert_foas_103115.pdf

- **Washington Department of Ecology – Laboratory ID C916**

  a) View at: http://www.eurofinsus.com/media/16070/washington1.pdf
  b) View at: http://www.eurofinsus.com/media/16069/washington2.pdf

APPENDIX F – LIST OF PHYSICAL LOCATIONS

F.1 Main Laboratory

- 7440 Lincoln Way, Garden Grove, CA 92841-1427
- 714-895-5494 Fax 714-894-7501

F.2 Satellite Laboratory 1

- 7445 Lampson Avenue, Garden Grove, CA 92841-2903
- Fax 714-898-2036

F.3 Satellite Laboratory 2

- 11380 Knott Street, Garden Grove, CA 92841-1400

F.4 Concord, CA Service Center

- 5063 Commercial Circle, Suite H, Concord, CA 94520-8577
- 925-689-9022 Fax 925-689-9023

APPENDIX G – SPECIAL PROGRAM REQUIREMENTS

F.1 United States Department of Defense / Energy Environmental Laboratory Accreditation Program

1. ECI participates and is accredited in the United States Department of Defense / Energy Environmental Laboratory Accreditation Program (DOD/DOE-ELAP).

2. The DOD/DOE ELAP will provide a means for laboratories to demonstrate conformance to the DOD/DOE Quality Systems Manual for Environmental Laboratories (DOD/DOE QSM) as authorized by DOD/DOE Instruction 4715.15, Environmental Quality Systems, December 2006 and as required by the DOD/DOE Policy and Guidelines for Acquisitions Involving Environmental Sampling or Testing, December, 2007. The DOD/DOE QSM is based on the National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems standard (Chapter 5), which provides guidelines for implementing the international standard, ISO/IEC 17025, General Requirements for the Competence of Testing and Calibration Laboratories.

3. The DOD/DOE ELAP will apply to environmental programs / projects at DOD/DOE operations, activities, and installations, including Government-owned, contractor-operated facilities and formerly used defense sites, where testing is being performed in support of environmental restoration programs. The program will apply to all laboratories, including permanent, temporary, or mobile facilities, that generate definitive data, regardless of their size, volume of business, or field of accreditation; the collection of screening data will be governed by project specific requirements.

4. The current DOD/DOE Quality Systems Manual for Environmental Laboratories is Version 5.0, dated June 2013

5. Implementation of the DOD/DOE Quality Systems Manual for Environmental Laboratories Version 5.0, dated July 2013, will be phased in over the 2014-2015 time period.

6. The ECI Management will provide sufficient training, resources and other measures to ensure compliance with the DOD/DOE QSM as appropriate. (including but not limited to):

    a. Specific Standard Operating Procedures (SOPs) and / or Appendicles
    b. DOD/DOE compliant Laboratory Information Management System (LIMS) analytical test codes
    c. Specialized technician and chemist training
    d. Enhanced Quality Assurance (QA) oversight
    e. Project specific instruments
    f. Assigned Project Management personnel
    g. Quality Assurance Project Plans (QAPP)
    h. DOD/DOE analytical data reporting qualifiers
    i. Calibration and reference materials that meet DOD/DOE requirements.

APPENDIX H – LISTING OF MAJOR ANALYTICAL INSTRUMENTATION

GC/MS SYSTEMS

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
GC/MS-K	HP 6890	US00024158	1998	Air	XP
	HP5973	US82311263	1998		
	Entech 7100A	0063	1998		
	Entech 7016CA	00142	1998		
GC/MS-L	HP 6890	US00023714	1998	Volatiles	XP
	Agilent 5973	US82311287	1998		
	Tekmar Atomx	US09163001	2009		
GC/MS-M	HP 6890	US00028876	1999	Volatiles	XP
	HP 5973	US9192601	1999		
	Tekmar Stratum	US08283015	2010		
	Varian Archon	MS0903W013	2010		
GC/MS-O	Agilent 6890N	US00034260	2000	LUFT-TPPH	XP
	Agilent 5973	US94240048	2000		
	Tekmar 3100	US02261003			
	Varian Archon	13863	2002		
GC/MS-P	Agilent 6890	US00034661	2000	Semivolatiles	XP
	Agilent 5973N	US94240038	2000		
	Agilent G2613A (Injector)	CN35234549	2000		
	Agilent G2614A (Tray)	US04109505	2000		
GC/MS-Q	Agilent 6890	US00037519	2000	Volatiles	XP
	Agilent 5973	US03340458	2000		
	Tekmar Stratum	US13099007	2013		
	Varian Archon	13386	2000		
GC/MS-R	Agilent 6890	US00037782	2000	Volatiles	XP
	Agilent 5973	US03340489	2000		
	Tekmar Stratum	US12111001	2012		
	Varian Archon	14040	2003		
GC/MS-S	Agilent 6890	US00030897	2000	Summa QC	XP
	Agilent 5973	US03340414	2000		
	Tekmar Autocan	US06047025	2006		
GC/MS-T	Agilent 6890	US00039185	2000	Volatiles	XP
	Agilent 5973	US03940628	2000		
	Tekmar Atomx	US11048001	2011		
GC/MS-U	Agilent 6890	US00036171	2001	Summa QC	XP
	Agilent 5973	US02450134	2001		
	Tekmar Autocan	US08169005	2002		
GC/MS-V	Agilent 6890	US00036172	2001	Air	XP

	Agilent 5973	US02450131	2001		
	Entech 7100A	1092	2005		
	Entech 7016CA	1041	2005		
GC/MS-W	Agilent 6890	US00036170	2001	Volatiles	XP
	Agilent 5973	US02450128	2001		
	Tekmar Stratum	US09154005	2010		
	Varian Archon	13573	2001		
GC/MS-X	Agilent 6890N	US10203064	2002	Air	XP
	Agilent 5973	US10462129	2002		
GC/MS-Y	Agilent 6890	US10203153	2002	Semivolatiles	XP
	Agilent 5973	US10442209	2002		
	Agilent G2613A (Injector)	US00211064	2002		
	Agilent G2614A (Tray)	CN64942239	2002		
GC/MS-Z	Agilent 6890N	US10225110	2002	Volatiles	XP
	Agilent 5973	US21842958	2002		
	Tekmar Stratum	US12115008	2012		
	Varian Archon	15278	2008		
GC/MS-AA	Agilent 6890N	US10225149	2002	Air	XP
	Agilent 5973N	US21843250	2002		
	Entech 7100A	1045	2003		
	Entech 7016CA	1183	2004		
	Entech 7016CA	1212	2004		
GC/MS-BB	Agilent 6890N	US1023004	2002	Volatiles	XP
	Agilent 5973N	US21843288	2002		
	Tekmar Stratum	US08283014	2012		
	Varian Archon	15208	2007		
GC/MS-CC	Agilent 6890N	US10233039	2002	Volatiles	XP
	Agilent 5973N	US21843272	2002		
	Tekmar Stratum	US10272001	2011		
	Varian Archon	13431	2002		
GC/MS-DD	Agilent 6890N	US10239018	2002	Air	XP
	Agilent 5973N	US21843913	2002		
	Entech 7100A	1432			
	Entech 7016CA	1018	2002		
	Entech 7016CA	1187			
GC/MS-EE	Agilent 6890N	US10248096	2003	Summa QC	XP
	Agilent 5973N	US21844395	2003		
	Tekmar Autocan	US99362027	1999		
GC/MS-GG	Agilent 6890N	CN10337014	2003	Marine Lab	XP
	Agilent 5973N	US33246020	2003		

	Agilent GC 80 SPME	CH00213565	2011		
GC/MS-HH	Agilent 6890N	CN10337015	2003	Air	XP
	Agilent 5973	US30945837	2003		
	Entech 7100A	1081	2003		
	Entech 7016CA	1012	2003		
	Entech 7016CA	1038	2003		
GC/MS-II	Agilent 6890	CN10517039	2005	Air	XP
	Agilent 5973	US44647341	2005		
	Entech 7100A	1458	2008		
	Entech 7016CA	1098	2005		
	Entech 7016CA	1225	2008		
GC/MS-JJ	Agilent 6890N	CN10547073	2005	Volatiles	XP
	Agilent 5973	US53941344	2005		
	Tekmar Stratum	US10230002	2010		
	Varian Archon	14529	2005		
GC/MS-KK	Agilent 6890	CN10545117	2005	Air	XP
	Agilent 5973	US53941343	2005		
	Entech 7100A	1221	2005		
	Entech 7016CA	1207			
	Entech 7016CA	1210			
GC/MS-LL	Agilent 6890N	CN10651084	2007	Volatiles	XP
	Agilent 5975B	US63214670	2007		
	Tekmar 3100	US01317008	2002		
	Varian Archon	MS0902W026	2006		
GC/MS-MM	Agilent 6890N	CN10651076	2007	Semivolatiles	XP
	Agilent 5975B	US62715103	2007		
	Agilent G2913A (Injector)	CN51825044	2007		
	Agilent G2614A (Tray)	CN51833057	2007		
GC/MS-NN	Agilent 7890A	CN10717056	2007	Air	XP
	Agilent 5975C	US71215995	2007		
	Entech 7100A	1291	2012		
	Entech 7016CA	1211			
	Entech 7150	45	2010		
	Entech 7410	138	2010		
GC/MS-OO	Agilent 7890A	CN10745139	2007	Volatiles	XP
	Agilent 5975C	US73317841	2007		
	Tekmar Stratum	US07277008	2009		
	Varian Archon	14697	2008		
GC/MS-PP	Agilent 7890A	CN10744086	2007	Volatiles	XP
	Agilent 5975C	US73317584	2007		

	Tekmar Stratum	US07277012	2009		
	Tekmar SOLATek	US09051008	2009		
GC/MS-QQ	Agilent 7890A	CN10742034	2007	Volatiles	XP
	Agilent 5975C	US71216778	2007		
	Tekmar Stratum	US07277018	2008		
	Tekmar SOLATek	US08032004	2008		
GC/MS-RR	Agilent 7890A	CN10730015	2007	Volatiles	XP
	Agilent 5975C	US73317844	2007		
	Tekmar Stratum	US08032004	2008		
	Tekmar SOLATek	US08032006	2008		
GC/MS-SS	Agilent 7890A	CN10803049	2007	Semivolatiles	XP
	Agilent 5975C	US80618497	2007		
	Agilent G2613A (Injector)	US81801206	2007		
	Agilent G2614A (Tray)	CN80246945	2007		
GC/MS-TT	Agilent 7890A	CN10806032	2007	Semivolatiles	XP
	Agilent 5975C	US80618456	2007		
	Agilent G2613A (Injector)	CN80246390	2007		
	Agilent G2614A (Tray)	CN80246936	2007		
GC/MS-UU	Agilent 7890A	CN10805004	2007	Volatiles	XP
	Agilent 5975C	US71215984	2007		
	Tekmar Stratum	US08087006	2008		
	Varian Archon	15287	2008		
GC/MS-VV	Agilent 7890A	CN10805094	2007	Volatiles	XP
	Agilent C5975	US80118376	2007		
	Tekmar 3100	US02203002	2001		
	Tekmar SOLATek	US09050003	2008		
GC/MS-WW	Agilent 7890A	CN10803015	2007	Volatiles	XP
	Agilent 5975C	US80118375	2007		
	Tekmar Atomx	US11034002	2011		
GC/MS-XX	Agilent 7890A	CN10815050	2008	Volatiles	XP
	Agilent 5975C	US80828968	2008		
	Tekmar Stratum	US14097001	2014		
	Varian Archon	15273	2008		
GC/MS-YY	Agilent 7890A	CN10814115	2008	Air	XP
	Agilent C5975	US80828967	2008		
	Entech 7100A	1431	2008		
	Entech 7016CA	1208	2008		
	Entech 7016CA	1214	2008		
GC/MS-ZZ	Agilent 7890A	CN10814050	2008	Air	XP
	Agilent 5975C	US80828953	2008		

	Markes TD-100	GB00K10173	2011		
GC/MS-AAA	Agilent 7890A	CN10812068	2008	Semivolatiles	XP
	Agilent 5975C	US80828988	2008		
	Agilent G2613A (Injector)	CN70438717	2008		
	Agilent G2614A (Tray)	CN64942222	2008		
GC/MS-BBB	Agilent 7890A	CN10947130	2009	Semivolatiles	XP
	Agilent 5975C	US93414124	2009		
	Agilent 7693 (Tray)	CN94701470	2009		
	Agilent 7693 (Injector)	CN11200098	2009		
GC/MS-CCC	Agilent 7890A	CN10947129	2009	Semivolatiles	XP
	Agilent 5975C	US93414097	2009		
	Agilent 7693 (Tray)	CN94901515	2009		
	Agilent 7693 (Injector)	CN95002678	2009		
GC/MS-DDD	Agilent 7890A	CN10031142	2009	Semivolatiles	XP
	Agilent 5975C	US10197302	2009		
	Agilent 7693 (Tray)	CN10210002	2009		
	Agilent 7693 (Injector)	CN10140077	2009		
GC/MS-EEE	Agilent 7890A	CN10241112	2009	Semivolatiles	XP
	Agilent 5975C	US10257401	2009		
	Agilent 7693 (Tray)	CN10210100	2009		
	Agilent 7693 (Injector)	CN10230009	2009		
GC/MS-FFF	Agilent 7890A	CN10391179	2010	Volatiles	XP
	Agilent 5975C	US10407502	2010		
	Tekmar Atomx	US10200002	2010		
GC/MS-GGG	Agilent 7890A	CN10401096	2010	Volatiles	XP
	Agilent 5975C	US10287508	2010		
	Tekmar Atomx	US10246002	2010		
GC/MS-HHH	Agilent 7890A	CN10521074	2010	Semivolatiles	Win 7
	Agilent 5975C	CN11030007	2010		
	Agilent 7693 (Tray)	US11077507	2010		
	Agilent 7693 (Injector)	CN11050288	2010		
GC/MS-III	Agilent 7890A	CN10521075	2010	Semivolatiles	Win 7
	Agilent 5975C	US11077506	2010		
	Agilent 7693 (Tray)	CN11030009	2010		
	Agilent 7693 (Injector)	CN11050291	2010		
GC/MS-JJJ	Agilent 7890A	CN11441070	2011	Semivolatiles	Win 7
	Agilent 5975C	US11447702	2011		
	Agilent 7693 (Tray)	CN11440045	2011		
	Agilent 7693 (Injector)	CN11390136	2011		
GC/MS-KKK	Agilent 7890A	CN11441059	2011	Air	Win 7
	Agilent 5975C	US11447704	2011		

	Entech 7100A	1384	2008		
	Entech 7016CA	1212	2008		
	Entech 7016CA	1183	2007		
GC/MS-LLL	Agilent 7890A	CN12031151	2012	Air	Win 7
	Agilent 5975C	US12097802	2012		
	Entech 7100A	1290	2012		
	Entech 7016CA	1041	2005		
GC/MS-MMM	Agilent 7890A	CN12261027	2012	Air	Win 7
	Agilent 5975C	US12262A09	2012		
	Markes TD-100	GB00k10257	2012		
GC/MS-NNN	Agilent 7890A	CN14073088	2014	Semivolatiles	Win 7
	Agilent 5975C	US14052222	2014		
	Agilent 7693 (Tray)	CN13500019	2014		
	Agilent 7693 (Injector)	CN14020017	2014		
GC/MS-OOO	Agilent 7890B	CN14103035	2014	Air	Win 7
	Agilent 5977A	US1410J201	2014		
	Entech 7200	1161	2014		
	Entech 7016D	1421	2014		

GC TRIPLEQUAD SYSTEMS

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
GC/TQ-1	Agilent 7890A	US11041024	2011	Marine Lab	Win 7
	Agilent 7000 TQ/MS	US11046401	2011		
	Agilent 7693 (Tray)	CN11030015	2011		
	Agilent 7693 (Injector)	CN11050297	2011		
GC/TQ-2	Agilent 7890A	US11291011	2011	Marine Lab	Win 7
	Agilent 7000 TQ/MS	US11196604	2011		
	Agilent 7693 (Tray)	CN11180027	2011		
	Agilent 7693 (Injector)	CN95002669	2011		

GC SYSTEMS

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
GC-1	HP 5890 Series II Detector(s): PID/FID	3310A48771	1987	LUFT-GRO	2000
	Tekmar 3100	US01362002	2004		
	Varian Archon	15301	2008		
GC-4	HP 5890 Detector(s): PID/FID	2750A17251	1989	LUFT-GRO	XP
	OI 4560	B239040			
	Varian Archon	13142	1999		

GC-8	HP 5890 Series II PID/FID	3033A31219	1990	LUFT-GRO	XP
	Tekmar 3100	US02249008	2002		
	Varian Archon	MS1010W015	2008		
GC-9	HP 5890 Series II Detector(s): FID/FID	3033A32951	1991	Semivolatiles	NT
GC-12	HP 5890 Series II Detector(s): FID/TCD	3118A35448	1991	Semivolatiles	NT
GC-13	HP 5890 Series II FID/TCD	3033A32929	1990	Air	XP
GC-14	HP 5890 Series II Detector(s): FPD	3126A36770	1991	Air	XP
GC-18	HP 5890 Series II Detector(s): PID/FID	3235A44156	1992	LUFT-GRO	2000
	EST Encon	512080906			
	Varian Archon	15307	2008		
GC-21	HP 5890 Series II Detector(s): PID/FID	3336A51475	1994	LUFT-GRO	XP
	Tekmar 3100	US02331005	2007		
	Varian Archon	MS0902W025	2008		
GC-22	HP 5890 Series II+ Detector(s): PID/FID	3336A61360	1994	LUFT-GRO	XP
	Tekmar 3100	US02233006	2008		
	Varian Archon	14699	2006		
GC-24	HP 5890 Series II+ Detector(s): PID/FID	3336A53949	1994	LUFT-GRO	2000
	Tekmar 3000	98194007	1998		
	Varian Archon	13864	2004		
GC-25	HP 5890 Series II+ Detector(s): PID/FID	2921A23805	1994	LUFT-GRO	XP
	Tekmar 3100	314009			
	Varian Archon	13470	2001		
GC-26	HP 6890 Detector(s): NPD/NPD	US00001017	1995	Semivolatiles	XP
	G1513A (Injector)	CN12620285	1995		
	G1514A (Tray)	US83304659	1995		
GC-29	HP 5890 Series II Detector(s): PID/FID	3310A47430	2000	LUFT-GRO	XP
	Tekmar 3100	US02249004	2002		
	Varian Archon	13874	2002		
GC-31	HP 6890 Detector(s): ECD/ECD	US00037979	2000	Semivolatiles	XP
	G2613A (Injector)	CN43138313	2000		
	G2614A (Tray)	CN71543642	2000		

GC-34	HP 5890 Series II Detector(s): FID	3033A32699	2000	Air	XP
GC-35	Agilent 6890N Detector(s): NPD/NPD	US10206061	2002	Semivolatiles	XP
	G2613A (Injector)	US81501043	2002		
	G2614A (Tray)	US83501663	2002		
GC-36	Agilent 6890N Detector(s): FID/TCD	US10346058	2004	Air	XP
GC-37	Agilent 6890N Detector(s): ECD/ECD	CN10350094	2004	Marine Lab	XP
GC-38	HP 5890 Series II Detector(s): FID	3029A30188	1995	Air	XP
GC-40	Agilent 7890N Detector(s): ECD/ECD	CN10647089	2007	Semivolatiles	XP
	G2913A (Injector)	CN715400009	2007		
	G2614A (Tray)	CN64842106	2007		
GC-41	Agilent 7890N Detector(s): ECD/ECD	CN10650013	2007	Semivolatiles	XP
	G2913A (Injector)	CN70538721	2007		
	G2614A (Tray)	CN43130148	2007		
GC-42	Agilent 6890N Detector(s): PID/FID	CN10647056	2007	LUFT-GRO	XP
	Tekmar 3100	US01274007			
	Varian Archon	14370	2004		
GC-43	Agilent 6890N Detector(s): FID	CN10720004	2007	Air	XP
GC-44	Agilent 6890N Detector(s): FID/FID	CN10721103	2007	Semivolatiles	XP
	G2913A (Injector)	CN71840418	2007		
	G2614A (Tray)	CN71843829	2007		
GC-45	Agilent 7890A Detector(s): FID/FID	CN10808107	2007	LUFT-DRO	XP
	G2913A (Injector)	CN81949025	2007		
	G2614A (Tray)	CN80747427	2007		
GC-46	Agilent 7890A Detector(s): FID/FID	CN1080815	2007	LUFT-DRO	XP
	G2913A (Injector)	CN81949036			
	G2614A (Tray)	US83201509			
GC-47	Agilent 7890A Detector(s): FID/FID	CN10819056	2008	LUFT-DRO	XP
	G2913A (Injector)	CN81748778	2008		
	G2614A (Tray)	CN81748307	2008		
GC-48	Agilent 7890A Detector(s): FID/FID	CN10819057	2008	LUFT-DRO	XP

	G2913A (Injector)	CN64837502	2008		
	G2614A (Tray)	CN64541796	2008		
GC-49	Agilent 7890A Detector(s): FID/FID	CN10820151	2008	LUFT-DRO	XP
	G2913A (Injector)	CN71549035	2008		
	G2614A (Tray)	CN82048589	2008		
GC-50	Agilent 7890A Detector(s): FID/FID	CN10820150	2008	LUFT-DRO	XP
	G2913A (Injector)	CN80546905	2008		
	G2614A (Tray)	CN82048581	2008		
GC-51	Agilent 7890A Detector(s): ECD/ECD	CN10822026	2008	Semivolatiles	XP
	G2913A (Injector)	CN82049336	2008		
	G2614A (Tray)	CN82148694	2008		
GC-52	Agilent 7890N Detector(s): FID	CN10824005	2008	Air	XP
GC-53	Agilent 6890N Detector(s): FID	US00002691	2000	Air	XP
GC-54	Agilent 7890A Detector(s): FPD	US10840051	2008	Air	XP
GC-55	Agilent 7890N Detector(s): TCD	CN10844112	2008	Air	XP
GC-56	Agilent 7890N Detector(s): FID	CN10847124	2009	LUFT-GRO	XP
	OI Eclipse	D647466449P			
	Varian Archon	15139	2007		
GC-57	Agilent 7890N Detector(s): ECD/ECD	CN10847113	2009	LUFT-GRO	XP
	OI Eclipse	D81466987P			
	Varian Archon	15140	2007		
GC-58	Agilent 7890N	CN10942196	2009	Semivolatiles	XP
	Agilent 7693 (Tray)	CN64937563	2009		
	Agilent 7693 (Injector)	CN81748311	2009		
GC-59	Agilent 7890N Detector(s): FID	CN10041127	2009	Air	XP
GC-60	Agilent 6890N Detector(s): FID	US10247091	2003	Air	XP
GC-61	Agilent 6890N Detector(s): FID	US00007963	1998	Air	XP
GC-62	Agilent 6890N Detector(s): FID	US00036172	2001	Air	XP
GC-63	Agilent 7890A Detector(s): ECD/ECD	CN12151152	2012	Marine	XP

GC-64	Agilent 6890A Detector(s): FID	US00030941	1999	Air	XP
GC-65	Agilent 7890A Detector(s): TCD	CN12111151	2012	Air	XP
GC-66	Agilent 7890A Detector(s): FID Agilent 7693 (Tray) Agilent 7693 (Injector)	CN12421146 CN12320016 CN12300140	2012	Semivolatiles	XP

Inductively Coupled Plasma Spectrophotometers (ICP)

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
ICP-7	PE Optima 7300 DV	077C8120401	2008	Metals	XP
	ESI SC FAST	4DX-F1-TSP	2013		
ICP-8	PE Optima 8300		2014	Metals	Win 7
	ESI SC4 optiFAST Dxi		2014		

Inductively Coupled Plasma/Mass Spectrometers (ICP/MS)

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
ICP/MS-3	PE ELAN DRC-e	AH 14610812	2009	Metals	XP
	ESI SC4 DX	X4DX5HSTSP16110413			
ICP/MS-4	PE ELAN DRC-e	AH 13440801	2009	Metals	XP
	ESI SC4 DX	X4DX5HSTSP16110603			
ICP/MS-5	PE NexION 300D	81DN1120502	2011	Metals	XP
	ESI SC4 DX	FST04-TSP-091203	2001		

Flame Atomic Absorption Spectrometers (FAA)

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
FAA-3	PE PinAAcle 900F	PFAS11090701	2011	Metals	Win 7

Mercury Analyzers

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
HG-4	PE FIMS-400	401S2030103	2005	Metals	XP
HG-5	PE FIMS-400	401S5070901	2005	Metals	XP
HG/AF-1	Teledyne Hydra II	1095	2011	Metals	Win 7

High Performance Liquid Chromatographs (HPLC)

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
HPLC-5	Variable Wave. Det.	JP116144U1	2001	Semivolatiles	XP

Agilent 1100 HPLC	Column Compartment	DE11120911	2001		
	Quat. Pump	DE11114727	2001		
	Degasser	JP05029389	2001		
	Autosampler	DE11115637	2001		
HPLC-6	Variable Wave. Det.	JP11414177	2001	Semivolatiles	XP
Agilent 1100 HPLC	Quat. Pump	DE11114712	2001		
	Degasser	JP05029404	2001		
	Autosampler	DE11115492	2001		
HPLC-7	Variable Wave. Det.	DE43602867	2004	Semivolatiles	XP
Agilent 1100 HPLC	Iso Pump	DE409006799	2004		
	Column Compartment	DE111210117	2004		
	Autosampler	DE33225927	2004		
Pickering	Pinnacle PCX	513305	2013		
HPLC-8	Multi. Wave. Det.	DE60555324		Semivolatiles	XP
Agilent 1200 HPLC	Iso Pump	DE62956826			
	Fraction Collector	DE60555134			
	Autosampler	DE63055195			

Liquid Chromatography/Mass Spectrometry (LC/MS/MS)

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
LC/TQ-1	Varian 1200L Triple Quad	3060	2005	Inorganics	XP
	Varian Prostar 210	4151	2005		
	Varian Prostar 210	4152	2005		
	Varian 410 Autosampler	50062	2005		
LC/TQ-2	Agilent 6430 LC/MS Triple Quad	SG11077104	2013	Inorganics	7
	Agilent 1260 Quat Pump	DEAB707001	2013		
	Agilent 1260 ALS	DEAAC17936	2013		
TOC-4	OI Soil Module Detector(s): IR	C339776273	2003	Inorganics	XP
TOC-5	OI Soil Module Detector(s): IR	C726776952	2007	Inorganics	XP
TOC-6	OI Aurora 1030	J025730749P	2011	Inorganics	XP
	OI 1088 A/S	J025730749P	2011		
TOC-8	OI Aurora 1030	N248731638P	2012	Inorganics	XP
	OI 1088 A/S	E248788640	2012		
IC-7	Dionex ICS-1000 Detector(s): Conductivity	3100486	2003	Inorganics (Anions)	XP
IC-8	Dionex ICS-2000 Detector(s): Conductivity	4100279	2004	Inorganics (Perchlorate)	XP

IC-9	Dionex ICS-1000 Detector(s): Conductivity	8120823	2008	Inorganics (Anions)	XP
IC-10	Dionex ICS-1000 Detector(s): Conductivity	8120822	2008	Inorganics (Anions)	XP
IC-11 Dionex ICS-3000	Variable Wave. Detector	8120958	2009	Inorganics (Cr(VI))	XP
	Single Pump	9010071	2009		
	Column Comp.	8120362	2009		
	AS-DV Autosampler	10100586	2009		
IC-12 Dionex ICS-3000	Variable Wave. Detector	9060673	2009	Inorganics (Cr(VI))	XP
	Single Pump	9060616	2009		
	Column Comp.	9010928	2009		
IC-13	Dionex ICS-1100 Detector(s): Conductivity	9120764	2009	Inorganics	XP
IC-14 Dionex ICS-5000	Variable Wave. Detector	9100584		Inorganics	XP
	Single Pump	10100152			
	Column Comp.	10100022			
	AS-DV Autosampler	10100586			
IC-15	Dionex ICS-1100 Detector(s): Conductivity	14038039	2014	Inorganics	XP
	AS-DV Autosampler	14037446	2014		
ACA1	OI 3360 Flow Analyzer Detector(s): UV	751893730	2007	Inorganics	XP
UV-4	Thermo Detector(s): UV	3DUK232006	2007	Inorganics	XP
UV-5	Thermo Detector(s): UV	3DUK228001	2007	Inorganics	XP
UV-7	Agilent 8453 Detector(s): Diode Array	CN22807187	2008	Inorganics	XP
UV-8	Agilent 8453 Detector(s): Diode Array	CN22808466	2010	Inorganics	XP
UV-9	Agilent 8453 Detector(s): Diode Array	CN22809400	2013	Inorganics	XP

FT-IR Spectrometer

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
IR-2	P.E. Spectrum Two	89327	2011	LUFT-DRO	Win 7

Automated Extractors

Designation	Manufacturer/Model	Serial Number	Acquired	Department
ASE-1	Dionex ASE-200	98120515	1999	Marine Lab
ASE-2	Dionex ASE-200	99090112	1999	Extractions

ASE-3	Dionex ASE-300	1100597	2002	Extractions
ASE-4	Dionex ASE-300	1100598	2002	Extractions
ASE-5	Dionex ASE-200	07040191	2007	Marine Lab
ASE-6	Dionex ASE-200	07010483	2007	Extractions
ASE-7	Dionex ASE-350	08080167	2010	Extractions
ASE-8	Dionex ASE-350	09020620	2010	Extractions
ASE-9	Dionex ASE-350	10090204	2012	Extractions
ASE-10	Dionex ASE-350	10090546	2012	Extractions

Solid Phase Extraction Unit

Designation	Manufacturer/Model	Serial Number	Acquired	Department
SPE-1	Horizon Tech/ 4790	11-1576	2010	Extractions
SPE-2	Horizon Tech/ 4790	11-1577	2010	Extractions
SPE-3	Horizon Tech/ 4790	11-1578	2010	Extractions
SPE-4	Horizon Tech/ 4790	11-1579	2010	Extractions
SPE-5	Horizon Tech/ 4790	11-1580	2010	Extractions
SPE-6	Horizon Tech/ 4790	11-1581	2010	Extractions
SPE-7	Horizon Tech/ 4790	11-1582	2010	Extractions
SPE-8	Horizon Tech/ 4790	11-1583	2010	Extractions

Misc. Shaker/Rotators

Designation	Manufacturer/Model	Serial Number	Acquired	Department
Rotator 7	Associated Design	3740-12BRE-11	?	Extractions
Rotator 9	Heidolf/REAX 20	120702298	?	Extractions
Rotator 3	Associated Design	1897	?	Extractions
Rotator 2	Associated Design	1282	?	Extractions
Rotator 8	Associated Design	2171	?	Extractions
Rotator 1	Associated Design	1697	?	Extractions
	Thermo MAXQ 2508	105253-3	?	Extractions
	Thermo MAXQ 3000	185905-68	?	Extractions
	Thermo MAXQ 3000	1411080905883	?	Extractions
	Southwest Sci. IncuShaker	1411080905883	?	Extractions
	Thermo MAXQ 3000	1411080398252	?	Extractions
	Thermo MAXQ 3000	141071288276	?	Extractions

Extraction Equip.

Designation	Manufacturer/Model	Serial Number	Acquired	Department
DVP001	Horizon DryVap Conc.	1131	?	Extractions
DVP001	Horizon DryVap Conc.	1377	?	Extractions

	Gerhardt SoxTherm	1803	2014	Extractions
	Gerhardt SoxTherm	1849	2014	Extractions
	Gerhardt SoxTherm	1555	2014	Extractions
	Gerhardt SoxTherm	2032	2014	Extractions
	FMS PowerVap Conc.	E-0235	2014	Extractions
	FMS PowerVap Conc.	E-0236	2014	Extractions

Particle Size Analyzer

Designation	Manufacturer/Model	Serial Number	Acquired	Department	OS
PSA-1	B.C. LS13320	AT39390	2011	Marine Lab	XP

Gas Mixer

Designation	Manufacturer/Model	Serial Number	Acquired	Department
Mixer 1	Environics Series 2000	1490	1995	Air
Mixer 2	Environics Series 2000	4618	2009	Air

Wet Chemistry

Designation	Manufacturer/Model	Serial Number	Acquired	Department
PH 1	Fisher Accumet Basic	176	1997	IO
PH 4	Fisher Accumet Basic	AB81210901	2004	IO
ISE1	Thermo Sci. Orion Star	E03578	2011	IO
SC 2	Amber Science 3082	108039	2001	IO
SC 5	Amber Science 2052	1106043	2011	IO
TUR 3	HF Scientific Micro 100	301269	2003	IO
IO 01	Fisher ISOTemp Oven	40300024	2005	IO
IO 07	Fisher ISOTemp 6509 Oven	1580080398315	2012	IO
IO 08	Fisher ISOTemp 6509 Oven	1580080398313	2012	IO
IO 10	Fisher ISOTemp 6509 Oven	613128-624	2013	IO
IO 13	Fisher ISOTemp 6509 Oven	612568-551	2013	IO
Thermo 01	Thermo Sci. FD1535M	152991101110630	2013	IO
BOD 1	Thermo Auto. 10060000	A0067	2003	IO
IC 04	Fisher 11-679-25C Incubator	2018080505659	2012	IO
Balance 13	Fisher A-250	25275	1997	IO
Balance 14	Ohaus E02140	11120030978	1998	IO
Balance 13	Sartorious ME 235P	16503597	2004	IO

	Fisher low temp incubator	2018080505659		IO

Referigerators/Incubators

Designation	Manufacturer/Model	Serial Number	Acquired	Department
	Fisher low temp incubator	2018080505659	?	IO
FG-23	True Manufacturing T-23	7251068	?	Extractions
FG-24	True Manufacturing T-23	1-3453096	?	Extractions
FG-25	True Manufacturing T-23	1-3496118	?	Extractions

Lab Water Systems

Designation	Manufacturer/Model	Serial Number	Acquired	Department
	Barnstead EasyPure RoDi	1332060134165		LUFT
	Barnstead Diamond RO	1266071286485		VOA
	Barnstead NANOpure 7143	491510-421		VOA
	Barnstead E-Pure D4641	1090090114250		IO
	Barnstead E-Pure D4641	229758-32		LUFT D

Glassware Drying Kilns

Designation	Manufacturer/Model	Serial Number	Acquired	Department
Kiln-1	LL Kilns DaVinci	T3427-D-480-3P	2013	
Kiln-2	LL Kilns DaVinci	090111-F-CKG	2012	

Misc. Ovens

Designation	Manufacturer/Model	Serial Number	Acquired	Department
VOA-1	VWR 1325F	4094404		VOA
VOA-2	VWR 1350FM	400503		VOA
VOA-3	VWR 1325F	6109006		VOA
IO-06	VWR 1350FM	1101302		VOA

IT Equip.

Designation	Manufacturer/Model	Serial Number	Acquired	Department
NAS-1	EMC CLARiiON Array	AMP00103500986	2010	Lincoln
NAS-2	EMC CLARiiON Array	AMP00103500987	2010	Lampson
	HP ProCurve switch 5406zl	SG04SU23M		Lampson
	HP ProCurve switch 5406zl	1NO30TI1YZ		Lincoln
	Cisco 3800 router	FTX1143A4GP		Lampson
	Cisco 3800 router	FTX1143A4GQ		Lincoln
Server	Dell PowerEdge R900	FQBFDF1		Lampson

Server	Dell PowerEdge R900	3T8TKH1		Lincoln
Server	Dell PowerEdge 2650	JZR6F61		Lincoln
Server	Dell PowerEdge 2950	8MJWKH1		Lincoln
Server	Dell PowerEdge R720	5JB2TW1		Lincoln
UPS Batt. B/U	APC Symetra LX	ZA0624031279		Lampson
UPS Batt. B/U	Powerware PW9170	660C120AAAAAAAP		Lincoln

END OF DOCUMENT

APPENDIX B

Analytical Laboratory Standard Operating Procedures

Title : **EPA METHODS 120.1 and 9050A / SM 2510 B: SPECIFIC CONDUCTANCE (at 25°C)**

Document No. : SOP-M702
Revision No. : 3.5
Supersedes : 3.4

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PROPRIETARY INFORMATION STATEMENT

Revision 3.5 changes are noted in bold italicized typeface and preceded by a "▸" marker.

APPROVED FOR RELEASE BY: _____ 12/04/13
MANAGEMENT **DATE**

_____ 12-04-13
QA DEPARTMENT **DATE**

1. ►METHOD IDENTIFICATION

1.1. EPA Methods 120.1 9050A / SM 2510 B: Specific Conductance (At 25°C).

2. ►APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface, and saline wastes, domestic and industrial aqueous wastes and acid rain.

2.2. ***Soil, solid and non-aqueous matrices may be analyzed using the extraction procedure noted in Section 14.3. and reported as a modified method, EPA 120.1(M) or SM 2510 B(M).***

3. DETECTION LIMITS

3.1. Reporting Limits:

Range	Reporting Limit
Detection - <1000	1 µmhos/cm
≥1000 - <10000	10 µmhos/cm
≥10000	100 µmhos/cm

4. SCOPE AND APPLICATION

4.1. The term *conductance* refers to the ability of a material to carry an electric current. Liquids that carry electric current are generally referred to as electrolytic conductors. A standard measure is created by defining the physical parameters of the measurement to be taken. This standard measure is referred to as the *specific conductance*. By convention, the conductivity of a solution is that which it exhibits at 25°C. This document provides the procedure for the measurement of specific conductance at 25°C.

5. METHOD SUMMARY

5.1. The specific conductance of a sample is measured directly on the sample at room temperature using a standardized self-contained conductivity meter that has the capability to automatically correct measurements to 25°C.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility***.

6.12. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence***.

6.13. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed

simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.14. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.15. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.16. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.17. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.18. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.19. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.20. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.21. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.22. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.23. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.24. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly

prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. INTERFERENCES

7.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing samples.

7.2. Platinum electrodes can degrade with usage and cause erratic results. The electrode should be replatinized or replaced when readings become erratic.

7.3. Care must be taken to avoid solution 'carry over'. The cell should be rinsed in a sample of the solution to be measured before the actual measurement is made.

7.4. Conduction in aqueous solutions is by ionic movement and increases with temperature. This change is expressed in percent per degree 'C' relative to 25°C and is called the slope of solution. The conductivity meter employed (VWR Scientific Model 2052B) has Automatic Temperature Compensation (ATC) for slope correction; therefore, sample results are automatically normalized to provide the specific conductance at 25°C.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Program Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDS) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Conductivity meter: temperature compensating, ***Amber Science Model 2052***, or equivalent.

9.2. Conductivity cell: dip-type, cell constant K=9.00-11.00, capable of measuring 1 to 200000 µmhos/cm.

9.3. ***Instrument Software***

9.3.1. ***None.***

9.4. ***Instrument Maintenance and Troubleshooting***

9.4.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.4.2. ***Additional information can be found in the user manual or operating guide for the specific instrument.***

9.5. Vials: 40 mL pre-cleaned, disposable.

9.6. Centrifuge.

9.7. Balance, top loading, ***calibrated, capable of weighing to the nearest 0.01 g.***

9.8. ***Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.***

9.9. Ultrasonic bath, ***VWR Scientific Aquasonic Model 550T or equivalent.***

9.10. Specimen Container, 120 mL pre-cleaned, disposable.

9.11. Graduated Cylinder, 50 mL.

9.12. Test Tubes: 17 mm x 100 mm, pre-cleaned, disposable.

9.13. ***0.45*** µm Filters.

9.14. Filtration apparatus.

10. ►REAGENTS AND STANDARDS

10.1. ***Reagents***

10.1.1. Reagent water: Free of interferants to less than 1 µmhos/cm.

10.1.2. ***All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. ***Standards***

10.2.1. ***Cell constant determination standard: One level at 50000 µmhos, commercially prepared, NIST traceable (e.g., Ricca 50000 µmhos at 25°C, or equivalent). Record ID number of standard used in the Instrument Maintenance logbook.***

10.2.2. Calibration check standards: Three levels between 100 and 10000µmhos range, commercially prepared, NIST traceable (e.g., Fisher 102, 994, and 9886 µmhos at 25°C, ***or equivalent***). Record ***ID*** number of standard used in the Specific Conductance logbook.

10.2.3. Second source standard: Mid-calibration standard level from a source different from that of the calibration check standards (e.g., Oakton 1413 µmhos at 25°C). Record ***ID*** number of standard in the Specific Conductance logbook.

10.2.3.1. ***The second-source standard will function as a Laboratory Control Sample (LCS).***

10.2.4. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. ***Aqueous samples should be collected in 125-mL high density polyethylene (HDPE) containers with Teflon-lined closures. Solid samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.***

11.2. ***Samples should be maintained in a chilled state, 0-6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions*** without preservation from the time of collection until analysis.

11.3. EPA 120.1: Samples shall be analyzed within 24 hours of collection for aqueous samples. Holding time may be extended to 28 days if sample is filtered with a 0.45 µm filter within the 24-hour holding time.

11.4. EPA 9050A and SM 2510 B: Samples shall be analyzed within 28 days of collection for aqueous samples.

11.5. EPA ***120.1(M) and SM 2510 B(M)***: Samples shall be analyzed within 28 days of collection for solid samples.

11.6. Additional sample handling information can be found in the Sample Control SOPs.

12. ►QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. All quality control data should be maintained and available for easy reference and inspection.

12.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 should be adhered to, unless superseded in this document.

12.4. The values of the calibration check standards and second source standard shall not differ from the expected values by more than 5%. If the percent difference (%D) is greater than 5%, effect corrective action and recheck calibration.

12.5. ***Event Based Quality Control (LCS)***

12.5.1. ***Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample (LCS).***

12.5.1.1. ***The second-source calibration check standard will be used as the LCS.***

12.6. ***Matrix Based Quality Control (Sample Duplicates)***

12.6.1. ***Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a sample duplicate.***

12.6.2. ***The acceptance criteria for sample duplicates are as follows:***

12.6.2.1. ***The RPD is ≤ 25%.***

12.6.2.2. ***When the RPD of the sample duplicate is at or within the established acceptance limit, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.***

12.6.2.3. ***If the RPD of the sample duplicate is*** greater than 25%, effect corrective action, recheck calibration and reanalyze any samples analyzed following the duplicate sample in question.

12.6.3. ***Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.***

12.6.4. A sample duplicate shall be analyzed for every batch of 20 samples ***or portion thereof.***

12.6.4.1. ***EPA 9050A requires one sample duplicate for every 10 samples or portion thereof.***

12.6.5. ***The sample in combination with the sample duplicate can be used to assess the precision of the analytical measurements. The measurement is expressed as the relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.2.***

12.7. Corrective Action

12.7.1. The analyst must immediately inform the Group Leader of all out of control situations for specific handling instructions.

12.7.2. The out-of-control event must be documented in detail on an "Out of Control Corrective Action" form and reviewed by the Group Leader. The Group Leader shall implement corrective action, list the specific procedures employed and their outcome on the corrective action form.

12.7.3. A copy of the completed "Out of Control Corrective Action" form must be included with all affected data packages.

12.7.4. The Group Leader should consult with the Operations Manager and/or Quality Assurance Manager regarding procedural inquiries and recommendations for method modification.

12.7.5. Modifications to the analytical process are approved by Management and the QA Department as documented in a revised SOP.

13. ►CALIBRATION AND STANDARDIZATION

13.1. ***Analytical Balance***

13.1.1. ***Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.1.2. ***If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.2. ***Top Loading Balance***

13.2.1. ***Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.2.2. ***If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.3. ***Conductivity Meter***

13.3.1. If not already on, switch ON the conductivity meter and allow it to warm up for a minimum of 10 minutes. Verify that the correct cell is properly installed. Set the function switch to "A.T.C. On." Set the range to 2 mS. When the function switch is at "A.T.C. ON" any reading displayed by the meter is at 25°C.

13.3.2. Shake calibration check standard container and fill three (3) clean vials at least 1/2 full with the standard. There are three (3) commercially available Fisher calibration check standards that the laboratory uses; namely, 100, 1000, and 10000 µmhos/cm. The analyst may use ***any*** one of the three (3) calibration check standards to calibrate the instrument.

13.3.2.1. ***For daily nano-pure water check, the standards at ~100 and ~1000 µmhos are both required.***

13.3.3. Dip the cell into the first standard vial. Agitate the cell in the solution to expedite temperature equilibration and to dislodge air bubbles trapped in the cell. Allow 15 seconds to pass for the cell to equilibrate to the solution. Withdraw the cell and dispose of excess solution. Do not touch or wipe off the cell.

13.3.4. Repeat step ***13.3.3.*** with the second standard vial.

13.3.5. Place the cell into the third or last standard vial for measurement. Measurement must be made as soon as the cell is dipped into the solution. Using the calibration tool or a small screwdriver, adjust the standardize control screw to produce a reading equal to the nominal value of the calibration check standard. If reading falls within acceptance criteria, the potentiometer setting does not need to be changed. If the instrument reading after calibration is less than or greater than 5% of the nominal value of the calibration check standard then instrument must be recalibrated.

However, if instrument still fails to meet the acceptance criteria of ±5% of the nominal value of the calibration check standard then corrective action shall be effected. Calibration check standard(s) may be replaced; cell may need cleaning, replatinizing or replacement; or, the meter itself may need to be serviced.

13.3.6. ***Repeat steps 13.3.2 through 13.3.5 using the second-source standard.***

13.3.6.1. ***NOTE: For solid sample analysis, the second-source standard must be put through the sonication process (Section 14.3) prior to being read.***

14. ►PROCEDURE

14.1. Determination of Cell Constant

14.1.1. The cell constant of the conductivity meter shall be determined every six months, at a minimum; or when the analyst suspects that the meter is not functioning properly. If the cell constant is not to be determined, proceed to Section ***14.2***.

14.1.2. Turn the conductivity meter on and allow it to warm up for a minimum of 10 minutes. Verify that the correct cell is properly installed. Set the function switch to "ATC On." Set the range to 2 mS. When the function switch is at "ATC ON" the display is adjusted to provide a 25°C reading.

14.1.3. Allow the container of ***50000*** µmhos (at 25°C) standard to equilibrate to ambient temperature.

14.1.4. Shake container and fill three (3) clean vials at least 1/2 full with the standard.

14.1.5. Dip the cell into the first standard vial. Agitate the cell in the solution to expedite temperature equilibration and to dislodge air bubbles trapped in the cell. Allow 15 seconds to pass for the cell to equilibrate to the solution. Withdraw the cell and dispose of excess solution. Do not touch or wipe off the cell.

14.1.6. Repeat step ***14.1.5.*** with the second standard vial.

14.1.7. Place the cell into the third or last standard vial. The measurement must be made as soon as the cell is dipped into the solution.

14.1.7.1. ***If the reading is ≥ 49500, no adjustment is necessary.***

14.1.7.2. ***If the reading is < 49500, use*** the calibration tool or a small screwdriver ***to*** adjust the standardize control screw to produce a reading equal to ***50000*** µmhos.

14.1.8. Change the function switch to the "Self Check" position and Range Selector to Range "B" to display the cell constant. The cell constant should read between 9.00 and 11.00. Record the information in the instrument maintenance logbook and label the meter with the cell constant reading,

date performed and analyst initial. Instrument is ready for calibration check and analysis.

14.1.9. If the cell constant reading is outside this acceptance range (K=9.00-11.00) the meter should be restandardized. If the reading still remains outside the range, then analyst shall effect further corrective action that may include replatinizing or replacing the cell, or having the instrument serviced.

14.1.10. The meter is now ready for sample measurements.

14.2. Aqueous sample preparation

14.2.1. Although the conductivity meter will correct for temperature differences, all refrigerated samples should be allowed to reach room temperature (23-27°C) prior to analysis.

14.2.2. Prepare a sample by shaking container and filling a clean vial at least 1/2 full, ***or pour ~ 20 mL into a clean, labeled specimen container***.

14.3. Solid Sample Preparation

14.3.1. Weigh ***20.00 ± 0.20*** g solid sample into a specimen container.

14.3.2. Add ***20*** mL of distilled water and mix with solid sample aliquot.

14.3.2.1. ***For LCS, measure 20 mL aliquots of second-source check standard (Section 10.2.3) into three separate containers***.

14.3.3. Ultrasonicate sample for ***30*** minutes.

14.3.4. Allow sample to sit for 10 minutes to separate supernatant from solid material.

14.3.5. If after sonication supernatant is turbid (cloudy), centrifuge sample for 15 minutes to obtain clear liquid.

14.3.6. Decant clear supernatant into a test tube ***or specimen container*** ready for analysis.

14.3.7. Perform analysis as per procedure in Section ***14.4***.

14.4. Sample Analysis

14.4.1. Rinse cell with one or more portions of the sample and immerse the cell into the sample vial a minimum of 1 1/2 inches. Agitate the cell in the solution to expedite temperature equilibration and also assist in the dislodging of air bubbles. Adjust the meter range accordingly and record the conductivity reading.

14.4.2. Repeat for each sample to be measured.

14.4.3. ***Samples are analyzed in the following or other logical order***.

1) Calibration check standard(s)
2) Second source standard ***(LCS)***
3) Samples (20 maximum)
4) Sample duplicate

14.4.3.1. ***Items 1 and 2: The calibration standards are used to check instrument performance. Acceptable readings demonstrate that the meter is operating properly. The calibration standards must be read prior to every batch of 20 samples or portion thereof.***

14.4.3.1.1. ***The second-source standard is used as the LCS.***

14.4.3.2. ***Item 3: Up to 20 samples per batch.***

14.4.3.3. ***Item 4: The sample in combination with the sample duplicate can be used to assess the precision of the analytical measurements. The measurement is expressed as the relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.2.***

15. CALCULATIONS

15.1. Calculations are not necessary to derive the specific conductance of a sample. The specific conductance is read directly from the display on the conductivity meter.

15.2. The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = Relative percent difference
C_1 = Original sample concentration
C_2 = Duplicate sample concentration

Note: Concentrations must be in equivalent units

15.3. The percent difference (%D) is calculated as follows:

$$\%D = \frac{(C_T - C_M)}{C_T} \times 100$$

where: %D = Percent difference
C_T = True standard concentration
C_M = Measured standard concentration

Note: Concentrations must be in equivalent units

15.4. Report analytical result as Specific Conductance, µmhos/cm, at 25°C.

15.5. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air-purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ***The second-source calibration check standard is used as the LCS. The %D from nominal value must be ≤ 5%.***

18.2. A duplicate sample shall be analyzed for every batch of 20 samples. The relative percent difference (RPD) between the original and duplicate results shall not exceed 25%. If the percent difference is greater than 25%, effect corrective action, recheck calibration and reanalyze any samples analyzed following the duplicate sample in question.

18.2.1. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. All concentrations shall be reported in µmhos/cm for water samples and µmhos/cm for oil, soil and solid waste samples based on a 1:1 deionized water extraction

18.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. ►REFERENCES

22.1. *2510B Conductivity, Laboratory Method*, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 ***(Committee approval 1997)***.

22.2. ***2510B Conductivity, Laboratory Method, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997/Edited 2011)***.

22.3. *Conductance, Method 120.1 (Specific Conductance, µmhos at 25°C),* Methods for Chemical Analysis of Water and Wastes, USEPA-600/4-79-020, March 1983.

22.4. *Method 9050A, Specific Conductance*, Test Methods for Evaluating Solid Waste (SW-846), Third edition, Volume 1C, USEPA, Revision 1, September 1996.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ***Appendix A: Resistivity by Calculation.***

23.2. ***Appendix B: Additional Quality Control Criteria for Department of Defense Projects***.

24. ►*MODIFICATIONS*

24.1. ***The following modifications from EPA Method 120.1 are noted.***

Calscience SOP M702 Section	Reference Document EPA 120.1 Section	Summary of Modification
14.3	8.0	Procedure for solid samples added.

24.2. ***The following modifications from SM 2510 B are noted.***

Calscience SOP M702 Section	Reference Document SM 2510 B Section	Summary of Modification
14.3	4b	Procedure for solid samples added.

25. ▶ *REVISION HISTORY*

Revision	Description	Author	Effective Date
3.5	Minor spelling/grammar corrections throughout. Section 1: Update method identification. Section 2: Update matrices. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample container and storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 22: Update references. Section 23: Add appendices. Section 24: Add Modifications. Section 25: Add Revision History.	K. Burney	12/16/2013

►*Appendix A*

RESISTIVITY BY CALCULATION

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ***EPA 120.1(M), Resistivity by Calculation.***

2. METHOD SUMMARY

2.1. ***EPA 120.1(M) is used to calculate resistivity from the specific conductance of the sample.***

3. EQUIPMENT AND SUPPLIES

3.1. ***Calculator, Scientific, Sper Scientific Calculator Model 830005 or equivalent.***

4. PROCEDURE

4.1. ***Data Interpretation***

4.1.1. ***Determine the resistivity from the specific conductance of the sample. The formula for calculating the resistivity is listed in Section 5.1. of this appendix.***

5. CALCULATIONS

5.1. ***The resistivity of a sample is calculated as follows:***

$$R = 1/SC$$

where: R = ***resistivity of sample in µohm-cm.***
SC = ***specific conductance of sample in µmhos/cm.***

5.2. ***All results shall be reported in µohm-cm for aqueous and solid samples.***

5.3. ***The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.***

6. REFERENCES

6.1. ***Conductance, Method 120.1 (Specific Conductance, µmhos at 25°C), Methods for Chemical Analysis of Water and Wastes, USEPA-600/4-79-020, March 1983.***

►*Appendix B*

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ***EPA Methods 120.1 and 120.1(M), 9050A / SM 2510 B and 2510 B(M): Specific Conductance (At 25°C) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.***

2. SCOPE AND APPLICATION

2.1. ***The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.***

3. STANDARDS

3.1. ***The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.***

4. QUALITY CONTROL

4.1. ***Limit of Detection (LOD)***

4.1.1. ***LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.***

4.1.2. ***LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.***

4.1.2.1. ***LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.***

4.1.2.2. ***LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).***

4.1.2.2.1. ***For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.***

4.1.2.3. ***If these criteria are not met, perform either one of the following tasks.***

4.1.2.3.1. ***Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.***

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. ***No samples shall be analyzed without a valid LOD.***

4.2. ***Limit of Quantitation (LOQ)***

4.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

4.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

4.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

4.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

4.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

4.2.2.2. ***LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

4.3. ***Event Based Quality Control (LCS)***

4.3.1. ***Laboratory Control Sample (LCS)***

4.3.1.1. ***The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."***

4.3.1.1.1. Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

4.3.1.2. ***The LCS shall be analyzed at a minimum frequency of one per preparation batch.***

4.3.1.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

4.3.1.3. ***The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.***

4.4. ***Matrix Based Quality Control (Sample Duplicates)***

4.4.1. ***Sample duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method.***

4.4.1.1. ***The sample duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.***

4.4.2. ***The frequency of the analysis of sample duplicates may be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the mandated test method.***

4.4.3. ***Each preparation batch of samples must contain an associated sample duplicate using the same matrix collected for the specific DoD project.***

4.4.3.1. ***In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.***

4.4.4. ***The results from sample duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments..***

4.4.5. ***Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.***

4.4.5.1. ***For sample duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.***

5. REFERENCES

5.1. ***Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.***

Title : **EPA METHOD 130.2 / SM 2340 C, HARDNESS, TOTAL (TITRIMETRIC, EDTA)**

Document No. : SOP-M721
Revision No. : 1.4
Supersedes : 1.3

PROPRIETARY INFORMATION STATEMENT

Revision 1.4 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 11/30/12
MANAGEMENT **DATE**

_____ 11-30-12
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 130.2 / SM 2340 C, Hardness, Total (Titrimetric, EDTA).

2. APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

3. DETECTION LIMITS

3.1. The estimated quantitation limit (EQL) for this method is 2.0 mg/L of $CaCO_3$.

4. SCOPE AND APPLICATION

4.1. Method 130.2 / SM 2340 C is used to determine the concentration ranges of hardness for sample aliquots containing no more than 25 mg of calcium carbonate.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of the instruments and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

5. METHOD SUMMARY

5.1. Ethylenediaminetetraacetic acid (EDTA) and its sodium salts form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the calcium and magnesium have been complexed, the solution turns from wine red to blue, marking the end point of the titration.

5.1.1. Magnesium ion must be present to yield a satisfactory end point. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

5.1.2. The sharpness of the end point increases with increasing pH. However, the pH cannot be increased indefinitely due to the danger of precipitating calcium carbonate or magnesium hydroxide, and due to the changes of dye color at high pH values. The specified pH of 10.0 ± 0.1 is a satisfactory compromise. In addition, a limit of 5 minutes is set for the duration of the titration to minimize the tendency toward calcium carbonate precipitation.

5.2. EPA Method 130.2 / SM 2340 C describes the procedure for the determination of total hardness as the concentration of calcium carbonate for an aqueous sample. Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is

detected by means of Eriochrome Black T or Calmagite indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

5.3. Prior to titration, wastewater and highly polluted water samples must be digested using the appropriate sample preparation methods. Acceptable preparatory methods include the following:

Sample Digestion	Method No.	SOP No.
Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA/ICP	EPA 3005A	M220
Acid Digestion of Aqueous Samples/Extracts for Total Metals for Analysis by FLAA/ICP	EPA 3010A	M223
Acid Digestion of Samples/Extracts for Total Metals by GFAA/ICP/MS	EPA 3020A	M221

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD) is defined as the smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99 %). At the LOD, the false negative rate (Type II error) is 1 %.***

6.12. ***Limit of Quantitation (LOQ) is at the lowest concentration that produces a quantitative result within specified limits of precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Terms Specific to Total Hardness Determination

6.27.1. Alkalinity: A measure of the acid-neutralizing capacity of a sample.

6.27.2. Carbonate Hardness: The amount of hardness that is numerically equal to or less than the sum of carbonate and bicarbonate alkalinity.

6.27.3. Hardness: A measure of the capacity of water to precipitate soap.

6.27.4. Non-carbonate Hardness: The amount hardness that is in excess of carbonate hardness.

6.27.5. Total Hardness: The sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligram per liter.

7. INTERFERENCES

7.1. Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

7.1.1. Routine addition of sodium cyanide solution to prevent potential metallic interference is recommended.

7.2. Suspended or colloidal organic matter may interfere with the end point.

7.2.1. Eliminate this interference by evaporating the sample to dryness on a steam bath and heating in a muffle furnace at 550°C until the organic matter is completely oxidized. Dissolve the residue in 20 mL of 1-N HCl, neutralize to pH 7 with 1-N NaOH, and adjust the volume to 50 mL with reagent water; cool to room temperature and continue according to the general procedure.

7.3. Conduct titrations at or near normal room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.

8. SAFETY

8.1. Sodium cyanide (NaCN) is a deadly poison and should be handled with extreme caution to avoid ingestion or skin and eye contact. Wash hands thoroughly after use and work only when a cyanide antidote kit is readily available. Immediate medical attention is required in the event of cyanide poisoning.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Specimen container, 4.5-oz (120-mL), with lid, plastic, disposable.

9.2. Volumetric flasks, 100-mL, 500-mL, and 1 L, Class A.

9.3. Graduated cylinder, 50-mL, Class A.

9.4. Buret, 50-mL, borosilicate glass, Class A.

9.5. Beaker, 100-mL, glass, Class A.

9.6. Pipetter, 100−1000-µL, adjustable, with disposable tip.

9.7. Pipetters, 500-µL and 1000-µL, fixed, with disposable tips.

9.8. Pipet, transfer, plastic, disposable.

9.9. Magnetic stirrer.

9.10. Stirring bar, Teflon.

9.11. Hot plate.

9.12. pH meter, Accumet Basic pH meter equipped with ATC probe, or equivalent.

9.13. pH paper, narrow range.

9.14. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.15. Balance, analytical, capable of weighing to the nearest 0.1 mg.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, distilled, deionized or nano-pure.

10.1.2. Buffer

10.1.2.1. Water hardness buffer, commercially prepared, certified, containing ammonium chloride, magnesium chloride hexahydrate, ammonium hydroxide, and disodium EDTA dihydrate, Fisher Scientific Catalog Number SB119-1 or equivalent.

10.1.3. Indicator

10.1.3.1. Eriochrome Black T ($C_{20}H_{12}O_7N_3SNa$) indicator, dry powder, commercially prepared, containing Eriochrome Black T and sodium chloride at 1% (w/w) ratio, Ricca Chemical Catalog Number 2900 or equivalent.

10.1.3.2. Calmagite ($C_{17}H_{14}O_5N_2S$) indicator, aqueous solution, commercially prepared, containing Calmagite and reagent water at 0.1% (w/v) ratio, Ricca Chemical Catalog Number 1830 or equivalent.

10.1.3.3. Methyl red ($C_{15}H_{15}N_3O_2$) indicator, aqueous solution. Prepare the indicator by dissolving 0.10-g $C_{15}H_{15}N_3O_2$ (reagent grade or equivalent) in reagent water, and dilute to 100 mL.

10.1.4. Inhibitor

10.1.4.1. Sodium cyanide (NaCN), granular, reagent grade or equivalent. Avoid contact with acid to prevent the release of highly toxic HCN gas.

10.1.5. Hydrochloric acid (HCl), 1:1 (v/v). Prepare the solution by diluting concentrated HCl (reagent grade or equivalent) with equal volume of reagent water.

10.1.6. Nitric acid (HNO_3), 1:1 (v/v). Prepare the solution by diluting concentrated HNO_3 (trace metals grade or equivalent) with equal volume of reagent water.

10.1.7. Calcium carbonate ($CaCO_3$), anhydrous, primary standard grade or equivalent.

10.1.8. Ammonium hydroxide (NH_4OH), concentrated, 28.0–30.0% (w/v) of NH_3 in H_2O, reagent grade or equivalent.

10.1.9. Ammonium hydroxide (NH_4OH), 3-N. Prepare the solution by diluting 210 mL of concentrated NH_4OH to 1 L with reagent water.

10.2. Standards

10.2.1. Standard EDTA titrant, 0.02-N, commercially prepared, certified, containing disodium salt of EDTA, Fisher Scientific Catalog Number SS221-4 or equivalent.

10.2.1.1. Store the titrant in polyethylene or borosilicate glass container to prevent extraction of hardness-producing cations from soft-glass container.

10.2.2. Standard calcium solution, 0.02-N, manually prepared.

10.2.2.1. Add sufficient amount of 1:1 HCl solution slowly to dissolve 1.0000-g $CaCO_3$ completely, and then add 200-mL reagent water.

10.2.2.2. Boil the solution for a few minutes to expel CO_2. Cool the solution, and then add a few drops of methyl red indicator.

10.2.2.3. Adjust the pH of the solution to the intermediate orange color with 1:1 HCl solution or 3-N NH_4OH solution.

10.2.2.4. Dilute the solution to 1 L with reagent water.

10.2.3. Reference standard calcium solution I, 10-mg/L of $CaCO_3$. Prepare the solution by diluting 1 mL of 0.02-N standard calcium solution to 100 mL with reagent water.

10.2.4. Reference standard calcium solution II, 100-mg/L of $CaCO_3$. Prepare the solution by diluting 10 mL of 0.02-N standard calcium solution to 100 mL with reagent water.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.2. Aqueous samples shall be preserved with 1 mL of 1:1 HNO_3 solution per 250 mL of sample.

11.2.1. Add preservation chemical to sample container prior to sample collection.

11.3. Samples should be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Upon receipt, the samples are stored in a 4°C cooler. Samples must be analyzed within 180 days of collection.

11.5. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. Reference Standards

12.1.1. One set of reference standards with two concentration levels must be analyzed daily prior to sample analysis and every batch of 20 samples or portion thereof.

12.1.2. The normality of standard EDTA titrant is deemed valid if the %D for each reference standard is ≤ 15%.

12.1.3. If these criteria are not met, then the standard EDTA titrant is unacceptable for sample analysis to resume. Investigate and effect corrective action, which may include replacement of the standard EDTA titrant.

12.2. Event Based Quality Control (MBs)

12.2.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB).

12.2.2. Ideally, the total hardness in an MB should be less than the respective reporting limit (RL). If the total hardness exceeds the RL, the source of contamination must be investigated and, if possible, eliminated.

12.2.3. A method blank consisting of reagent water should be analyzed for every batch of 20 samples or portion thereof. The method blank shall be carried through the entire analytical process.

12.3. Matrix Based Quality Control (Sample Duplicates)

12.3.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a sample duplicate.

12.3.2. The acceptance criteria for sample duplicates are as follows:

12.3.2.1. The RPD is ≤ 25%.

12.3.2.2. When the RPD of the sample duplicate is at or within the established acceptance limit, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.3.2.3. If the RPD of the sample duplicate is not within the established acceptance limits, the analytical system performance shall be suspect.

12.3.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

12.3.4. A sample duplicate should be analyzed for every batch of 20 samples or portion thereof. The sample in combination with the sample duplicate can be used to assess the precision of the analytical measurements. The measurement is expressed as the relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.3.

12.4. If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-analyzed.

12.5. Additional information regarding internal quality control check is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Analytical Balance

13.2.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.2.2. Calibration shall be within ± 10% at 2 mg (± 0.2 mg), or within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.3. Pipetter

13.3.1. Calibrate the pipetter using an analytical balance.

13.3.2. Calibration shall be within 5% (or 1% for standard pipetter) difference of the expected volume assuming the density of tap water is 1.000 g/mL. If the percent difference is not within the range, repair or replace the pipetter.

13.4. pH Meter

13.4.1. Calibrate the pH meter at pH of 4.00, 7.00, and 10.00 using fresh buffer solutions according to the instrument manufacturer's recommended procedures.

13.4.2. Verify the calibration with fresh second source buffer solution. The second source buffer shall not differ from its expected value by more than 0.05 pH

unit. If this criterion is not met, determine the cause of the problem, effect corrective action, and recalibrate.

13.5. Titrant Standardization

13.5.1. Transfer 50 mL of 0.02-N standard calcium solution into a beaker.

13.5.2. Add 2 mL of water hardness buffer and appropriate amount of Eriochrome Black T or Calmagite indicator to the standard calcium solution.

13.5.3. Titrate by adding standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add last few drops at 3−5 second intervals. At the end point, the color of the solution is blue. Titration should be completed within 5 minutes.

13.5.4. Calculate the normality of titrant. The formula for calculating normality is listed in Section 15.1.

13.5.5. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

13.5.5.1. Verify the normality of titrant with fresh 0.02-N standard calcium solution if the reference standard criteria listed in Section 12.1.2. are not met.

14. PROCEDURE

14.1. Pretreatment

14.1.1. Determine and record the pH of sample.

14.1.2. For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary.

14.1.3. For most wastewaters and highly polluted waters, the sample must be digested as specified in Section 5.3.

14.2. Determine the hardness level of sample through practice run.

14.3. Sample Titration

14.3.1. Transfer 50 mL of sample into a specimen container.

14.3.1.1. For method blank, transfer 50 mL of reagent water.

14.3.1.2. For reference standard I, transfer 50 mL of 10-mg/L reference standard.

14.3.1.3. For reference standard II, transfer 50 mL of 100-mg/L reference standard.

14.3.1.4. The amount of sample analyzed should require less than 50 mL of standard EDTA titrant.

14.3.2. Add 2 mL of water hardness buffer to the sample.

14.3.2.1. Use pH paper to check the pH. If the pH is not within 10.0 ± 0.1, adjust the pH with additional water hardness buffer.

14.3.3. Add inhibitor to the sample prior to the addition of indicator if interfering metal ions are suspect to be present.

14.3.3.1. Add 250-mg NaCN if metal ions interfere by causing fading or indistinct end points.

14.3.4. Add appropriate amount of Eriochrome Black T or Calmagite indicator to the sample.

14.3.5. Titrate by adding standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add last few drops at 3–5 second intervals. At the end point, the color of the solution is blue. Titration should be completed within 5 minutes.

14.3.5.1. If the volume of standard EDTA titrant exceeds 50 mL, dilute the sample with reagent water. Titrate the diluted sample and record the dilution factor.

14.3.6. Record the volume of standard EDTA titrant used to the nearest 0.1 mL.

14.4. Data Interpretation

14.4.1. Determine the total hardness of a sample from the normality of standard EDTA titrant, the volume of standard EDTA titrant used, and the volume of sample used. The formula for calculating the total hardness is listed in Section 15.4.

14.4.2. Determine the maximum concentrations of interferences permissible (see Appendix A) for interference correction.

15. CALCULATIONS

15.1. The normality of standard EDTA titrant is calculated as follows:

$$N_{EDTA} = \frac{N_{Ca} \times V_{Ca}}{V_{EDTA}}$$

where: N_{EDTA} = normality of standard EDTA titrant.
N_{Ca} = normality of standard calcium solution.
V_{Ca} = volume of standard calcium solution used in mL.
V_{EDTA} = volume of standard EDTA titrant used in mL.

15.2. The percent difference of total hardness is calculated as follows:

$$\%D = \frac{\left|C_{prepared} - C_{measured}\right|}{C_{prepared}} \times 100$$

where: %D = percent difference.

$C_{prepared}$ = total hardness as prepared.
$C_{measured}$ = total hardness as measured.

Note: Total hardnesses must be in equivalent units.

15.3. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = total hardness in measurement 1.
C_2 = total hardness in measurement 2.

Note: Total hardnesses must be in equivalent units.

15.4. The total hardness for a sample is calculated as follows:

$$H = \frac{N_{EDTA} \times V_{EDTA} \times 50000}{V_{sample}} \times D$$

where: H = total hardness of sample in mg/L of $CaCO_3$.
N_{EDTA} = normality of standard EDTA titrant.
V_{EDTA} = volume of standard EDTA titrant used in mL.
V_{sample} = volume of sample used in mL.
D = dilution factor (if no dilution was made, D = 1).

15.5. Total hardness shall be reported as mg/L (ppm) of $CaCO_3$ for aqueous sample.

15.6. Report total hardness which is < 10 mg/L to 2 significant figures, and total hardness which is ≥ 10 mg/L to 3 significant figures.

15.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the total hardness of an MB should be less than the respective reporting limit (RL). If the total hardness exceeds the RL, the source of contamination must be investigated and, if possible, eliminated.

18.2. The acceptance criteria for the RPD of the sample duplicate is ≤ 25%.

18.2.1. When the RPD of the sample duplicate is at or within the established acceptance limit, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.2.2. If the RPD of the sample duplicate is not within the established acceptance limits, the analytical system performance shall be suspect.

18.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

18.4. Additional information regarding internal quality control checks is provided in SOP-T020.

18.5. Total hardness shall be reported as mg/L (ppm) of $CaCO_3$ for aqueous sample.

18.6. Report total hardness which is < 10 mg/L to 2 significant figures, and total hardness which is ≥ 10 mg/L to 3 significant figures.

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. EPA Method 130.2: Hardness, Total (Titrimetric, EDTA), Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.2. 2340 C. Hardness, EDTA Titrimetric Method, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Maximum Concentrations of Interferences Permissible with Sodium Cyanide Inhibitor.

23.2. Appendix B: General Inorganic Raw Data Form – MBDUP (01/31/11).

24. ►MODIFICATIONS

24.1. The following modifications from EPA 130.2, ASTM 2340C are noted.

Calscience SOP M721 Section	Reference Document EPA 130.2, ASTM 2340C Section	Summary of Modification
12	QC	Added QC elements.

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
1.3	SOP revision.	E. Ng	03/07/07
1.4	SOP revision.	L. Lem	12/10/12

Appendix A

Maximum Concentrations of Interferences Permissible with Sodium Cyanide Inhibitor

Inhibitor (NaCN)	
Interfering Substance	**Maximum Interference Concentration (mg/L)[a]**
Aluminum	40
Barium	b
Cadmium	b
Cobalt	over 40
Copper	over 60
Iron	over 60
Lead	b
Manganese (Mn^{2+})	b
Nickel	over 40
Strontium	b
Zinc	b

[a] The concentration is based on 50-mL sample.
[b] Titrate as hardness.

Appendix B

GENERAL INORGANIC RAW DATA FORM – MBDUP

Calscience Environmental Laboratories
General Inorganic Raw Data Form – MBDUP

Analyte: ☐ Chlorine, Free, ☐ Chemical Oxygen Demand (COD), ☐ Organic Nitrogen, ☐ Oil and Grease, Total Recoverable, ☐ Sulfide, ☐ Sulfite,
☐ Other (Specify) _____

MB DUP

Instructions:

1. A copy of the supporting raw data must be attached.
2. Cel ID consists of Work Order Number and Container ID.

METHOD	MATRIX	DATE	ANALYST(S)	BATCH NUMBER	CONC UNIT(S)	INSTRUMENT NAME / ID
		Preparation:		MB:		
		Analysis:		Sample Duplicate:		

CEL ID #	INITIAL CONC	FINAL CONC	DILUTION FACTOR	PREP FACTOR	RPD	CONTROL LIMIT	COMMENTS
Sample						0 – 25	
Duplicate							

CEL ID #	TIME		SAMPLE				INITIAL CONC	FINAL CONC	FINAL RL	QUALIFIER	COMMENTS
	START	END	INITIAL WEIGHT / VOLUME	FINAL VOLUME	DILUTION FACTOR	PREP FACTOR					
MB											
Duplicate											

Title : **EPA METHOD 200.7, INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROMETRIC (ICP-AES) METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES**

Document No. : SOP-M624
Revision No. : 1.0
Supersedes : 0.0

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PROPRIETARY INFORMATION STATEMENT

Revision 1.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 06/07/13
MANAGEMENT **DATE**

_____ 06-07-13
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 200.7, Inductively Coupled Plasma – Atomic Emission Spectrometric (ICP-AES) Method for Trace Element Analysis of Water and Wastes.

2. APPLICABLE MATRICES

2.1. This method is applicable to drinking water, surface water, domestic and industrial wastewaters, and groundwater samples.

3. DETECTION LIMITS

3.1. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions.

3.2. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

4. SCOPE AND APPLICATION

4.1. Method 200.7 is used to determine dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters. Except groundwater samples, all aqueous matrices require acid digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards.

4.1.1. This method is not suitable for the determination of silica in solids.

4.2. For reference where this method is approved for use in compliance monitoring programs such as Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA), consult the appropriate sections of the Code of Federal Regulation Title 40 (40 CFR) and the latest Federal Register announcements.

4.2.1. For National Pollutant Discharge Elimination System (NPDES), consult 40 CFR Part 136 §136.3 Table 1B.

4.2.2. For drinking water, consult 40 CFR Part 141 §141.23.

4.3. The method can be used to determine dissolved analytes in filtered and acidified aqueous samples. To reduce potential interferences, the dissolved solids content of the sample should be < 0.2% (w/v).

4.4. For the determination of total recoverable analytes in aqueous and solid samples, appropriate digestion procedures are required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be digested as a solid type sample.

4.4.1. Since digestion techniques increase the dissolved solids content of the sample, appropriate steps must be taken to correct for potential interference effects.

4.5. With the exception of silver, where this method is approved for the determination of certain metals and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis." However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria.

4.6. When determining boron and silica in aqueous samples, only plastic, polytetrafluoroethylene (PTFE) or quartz labware should be used from the time of sample collection to the completion of analysis. For accurate determination of boron in solid samples, only quartz or PTFE beakers should be used during acid digestion with immediate transfer of a digestate aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

4.7. Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, matrix spikes and even laboratory control samples if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason, it is recommended that samples be digested prior to the determination of silver.

4.8. The method is applicable to the elements listed in Appendix A. Appendix A also lists the recommended analytical wavelengths and estimated instrument detection limits for the elements in clean aqueous matrices with insignificant background interferences. Elements and matrices other than those listed in Appendix A may be analyzed by this method if performance at the concentrations of interest (see Section 12.) is demonstrated.

4.9. Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruments provided by the manufacturer of the particular instruments.

4.10. This method is restricted to use by or under the supervision of analysts experienced in the use of inductively coupled plasma emission spectrometer, skilled in the interpretation of atomic emission spectra, and knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

5. METHOD SUMMARY

5.1. EPA Method 200.7 describes the simultaneous or sequential multi-elemental determination of trace elements in solution. The basis of the method is the

measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the resulting aerosol is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system.

5.2. Background correction is required to compensate for variable background contribution to the determination of trace elements. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Section 7. should also be recognized and appropriate corrections made. Alternatively, multivariate calibration methods may be utilized. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

5.3. ►Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods ***as outlined in Section 14.1***.

5.4. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. ►Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.***

6.13. ►***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Term Specific to ICP-AES Analysis

6.28.1. Dissolved Elements: The concentration of elements in a sample after the sample has been filtered through a 0.45-µm filter (EPA Method 3005A).

6.28.2. Linear Dynamic Range: The concentration range over which the analytical curve remains linear.

6.28.3. Method of Standard Addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard.

6.28.4. Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

6.28.5. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.28.6. Sensitivity: The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

6.28.7. Suspended Elements: The concentration of elements in the portion of sample that is retained by a 0.45-µm filter (EPA Method 3005A).

6.28.8. Total Elements: The concentration of elements determined in an unfiltered sample following digestion by EPA Method 3010A, or the sum of the dissolved and suspended concentrations.

6.28.9. Total Recoverable Elements: The concentration of elements in an unfiltered sample following treatment with hot, dilute mineral acid (EPA Method 3005A).

7. INTERFERENCES

7.1. Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

7.1.1. Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate

when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

7.1.2. To determine the appropriate location for off-line background correction, the analyst must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100-mg/L single-element solutions are sufficient. However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range.

7.1.3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Analysts may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Appendix B. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

7.1.4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al. According to Appendix B, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 0.01085 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.001085 mg/L. The analyst is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Appendix B. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

7.1.5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Analysts should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

7.1.6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (see Appendix B) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst shall utilize a computer routine for automatic correction on all analyses.

7.1.7. Analysts using sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

7.1.8. If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the

interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank, the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

7.1.9. When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for 5 consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

7.1.10. When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

7.1.10.1. One method is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

7.1.10.2. Another method is to analyze an interference check solution which contains similar concentrations of the major components of the samples (> 10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥ 20% of the analyte concentration, the analyte must be determined (1) using analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

7.2. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and

causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The dilution test (see Section 12.12.) will help determine if a physical interference is present.

7.3. Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

7.3.1. The MSA should be used if an interference is suspected or a new matrix is encountered. When the MSA is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences.

7.3.2. An alternative to using the MSA is to use the internal standard technique. Add one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium is often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

7.4. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to equal to or less than the method detection limit should be noted. Until the required rinse time is established, it is suggested that the rinse period be at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse

period of sufficient length. Alternate rinse times may be established by the analyst based upon the project specific data quality objectives (DQOs).

7.5. Analysts are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

7.6. The dashes in Appendix B indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

7.7. The calibration blanks (Section 10.2.3.1.) may restrict the sensitivity of the detection limit or degrade the precision and accuracy of the analysis. Clean chemistry methods and procedures are necessary in reducing the magnitude and variability of the calibration blank.

8. SAFETY

8.1. All sample preparation activities should be performed in an operational fume hood appropriate for use with acids.

8.2. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric buildup.

8.3. Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Inductively Coupled Argon Plasma Emission Spectrometer: Perkin-Elmer Optima 4300/5300 DV Optical Emission Spectrometer or equivalent configured with the following equipments:

9.1.1. Computer-controlled emission spectrometer with background correction.

9.1.2. Radio-frequency (RF) generator compliant with FCC regulations.

9.1.3. Mass-flow controller for argon nebulizer gas supply.

9.1.4. Peristaltic pump.

9.1.5. Autosampler, Perkin-Elmer AS 90 or equivalent.

9.1.6. Argon gas supply, high purity.

9.1.7. Nitrogen gas supply, high purity, for purge only.

9.1.8. PC based data system or equivalent.

9.2. ►***Instrument Software***

9.2.1. ***PerkinElmer WinLab32 for ICP Version 3.4.0.0253 or equivalent.***

9.3. ***Instrument Maintenance and Troubleshooting***

9.3.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.4. Volumetric flasks, 100-mL, 500-mL, and 1000-mL, Class A.

9.5. Pipetters, 10−100-µL, 100−1000-µL, 0.5−5.0-mL, and 1−10-mL, adjustable, with disposable tip.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Hydrochloric acid, HCl, concentrated, trace metals grade for equivalent.

10.1.2. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.2.1. Prepare the solution by slowly adding 500 mL of concentrated HCl to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.3. Nitric acid, HNO_3, concentrated, trace metals grade for equivalent.

10.1.4. Nitric acid, HNO_3, 1:1 (v/v).

10.1.4.1. Prepare the solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.5. Rinse blank, HCl-HNO_3-H_2O, 1:1:8 (v/v/v).

10.1.5.1. Prepare the rinse blank by slowly adding 1 part of concentrated HCl and 1 part of concentrated HNO_3 to 8 parts of reagent water.

10.1.5.2. The rinse blank consists of 10% (v/v) HCl and 10% (v/v) HNO_3 in reagent water.

10.1.5.3. The rinse blank is used to flush the system between standards and samples to minimize memory interferences (see Section 7.4.).

10.1.6. Reagent water, interferant free.

10.1.7. Chips, Teflon.

10.1.8. Beads, glass.

10.1.9. ►All reagents must be inspected and documented ***in the Chemicals and Supplies Verification Logbook*** prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions (ultra-high purity grade or equivalent), each in sealed polyethylene bottles, containing various concentrations of target analytes are used to prepare calibration and check standards.

10.2.1.2. Prior to preparing the calibration or check standards, analyze each stock standard solution separately to determine possible spectral interference or the presence of impurities.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Prepare the initial calibration standard solutions by combining appropriate volumes of the stock standards in volumetric flasks (refer to Appendix C for preparation).

10.2.2.2. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates.

10.2.2.2.1. If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days, if protected from the light. Higher concentrations of silver require additional HCl.

10.2.2.3. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together.

10.2.2.4. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage.

10.2.3. Blanks

10.2.3.1. Calibration Blank (CB)

10.2.3.1.1. Prepare the CBs by acidifying reagent water to the same concentrations of the acids found in the standards and samples.

10.2.3.1.2. The CB consists of 5% (v/v) HCl and 6% (v/v) HNO_3 in reagent water.

10.2.3.1.3. The CB is used to establish the zero point of the calibration curve.

10.2.3.1.4. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.3.2. Method Blank (MB)

10.2.3.2.1. Prepare the MBs using the appropriate sample preparation methods (see Section 5.3.).

10.2.3.2.2. The MB is used to identify possible contamination resulting from either the acids or the equipment used during sample processing including filtration.

10.2.3.3. Both CB and MB are required for the analyses of samples prepared by any method other than EPA Method 3040A.

10.2.4. Initial Calibration Verification (ICV) Solutions

10.2.4.1. Prepare the ICV solutions in the same acid matrix by combining compatible elements from a source differing from that used for the initial one-point calibration, and at a concentration within the established linear dynamic range (refer to Appendix C for preparation and Section 12.3. for evaluation).

10.2.5. Continuing Calibration Verification (CCV) Solutions

10.2.5.1. Prepare the CCV solutions by diluting initial calibration standards with equal volume of reagent water (refer to Section 12.7. for evaluation).

10.2.5.2. The CCV solutions contain mid-point concentration of each target analyte.

10.2.6. Internal Standard Solution

10.2.6.1. Prepare the internal standard solution in the same acid matrix (refer to Appendix C for preparation).

10.2.6.2. The internal standard contains 5 ppm each of Ho, Tb, and Y. It is used to reduce or overcome interferences (see Section 7.2. and Section 7.3.).

10.2.7. Potential Interference Check Solution

10.2.7.1. Prepare the potential interference check solution in the same acid matrix.

10.2.7.2. The potential interference check solution contains 200 ppm each of Al, Ca, Cr, Cu, Fe, Mg, Mn, Tl, and V. It is used to establish the potential interference table (see Section 12.1.).

10.2.8. Daily Spectral Interference Check Solutions (ICS-A and ICS-AB)

10.2.8.1. Prepare the daily spectral interference check solutions in the same acid matrix (refer to Appendix C for preparation and Section 12.6. for evaluation).

10.2.8.2. The ICS-AB and ICS-A solutions contain known concentrations of interfering elements. They are used to verify the interelement correction factors.

10.2.9. Spike Standard Solutions

10.2.9.1. Prepare the spike standard solutions in the same acid matrix by combining compatible elements from a source differing from that used for the initial one-point calibration, and at a concentration within the established linear dynamic range (refer to Appendix C for preparation).

10.2.9.2. The spike standard solutions are used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

10.2.9.3. Add 250 µL of the spike standard to each 5-mL aliquot of MS/MSD leachate (TCLP/SPLP/WET extract) prior to dilution and acidification.

10.2.9.4. Add 250 µL of the spike standard to each 50-mL aliquot of MS/MSD and LCS/LCSD sample prior to digestion.

10.2.9.5. Add 50 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

10.2.10. Linear Dynamic Range Solutions

10.2.10.1. Prepare a minimum of three different concentrations of the linear dynamic range solutions in the same acid matrix by diluting the spike standard solutions or the stock standard solutions. The analyst determines the applicable concentrations.

10.2.10.2. The linear dynamic range solutions contain various concentrations of compatible elements. They are used to establish linear dynamic range (see Section 12.5.).

10.2.11. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

10.2.11.1. The stability of low level standards (i.e., < 1 ppm), must be demonstrated prior to use.

10.2.11.2. Prepare fresh standards as needed.

10.2.12. ►All stock standards must be inspected and documented ***in the Chemicals and Supplies Verification Logbook*** prior to use.

10.3. ►***Solutions may be prepared in final volumes other than those noted, provided that correct ratios of all components are maintained.***

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene containers with Teflon-lined closures. Soil samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.

11.1.1. Aqueous samples for the determination of dissolved elements shall be filtered through a 0.45-µm effective pore size membrane filter at the time of collection or as soon thereafter as practically possible. Collect and acidify the filtrate with 1:1 HNO_3 solution to pH < 2.

11.1.2. Aqueous samples for the determination of total recoverable elements shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2. ►Samples should be maintained in a chilled state***, 0-6°C, not frozen,*** post sample collection until received at the laboratory, ***where they are stored under refrigerated conditions***.

11.2.1. Aqueous samples not acid preserved at the time of collection due to safety concerns, transport restrictions, or possible contamination must be returned to the laboratory within two weeks of collection, and preserved with 1:1 HNO_3 solution to pH < 2 upon receipt in the laboratory for at least 24 hours prior to metals analysis, except boron, chromium VI, and mercury analysis.

11.3. Refer to Appendix D for additional information on sample holding time, digestion volumes and suggested collection volumes.

11.3.1. The sample amount required depends upon the sample preparation procedures (i.e. leaching and digestion) necessary for the analysis.

11.3.2. The pH of all aqueous samples must be tested immediately prior to solubilization, digestion, or "direct analysis" to ensure that the samples have been properly preserved.

11.3.2.1. If for some reason, such as high alkalinity, the sample pH is verified to be > 2, more acid must be added and the sample held for 24 hours until verified to be pH < 2.

12. QUALITY CONTROL

12.1. Potential Interference Table

12.1.1. Following the initial instrument setup, the potential interference table (see Appendix B) must be established prior to initial calibration.

12.1.1.1. The potential interference table is established by analyzing the potential interference check solution (see Section 10.2.7.).

12.1.2. The potential interference table should be updated annually, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.2. Initial Calibration (IC)

12.2.1. The initial one-point calibration must be established daily prior to the processing of samples.

12.2.1.1. The calibration curve is established with one calibration blank and one high-level calibration standard.

12.2.2. The IC is deemed valid if the %RSD for each analyte is ≤ 5%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.3. ►Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ ***5***%.

12.3.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibration, if necessary.

12.4. Initial Calibration Blank (ICB)

12.4.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > RL (or the limit specified in the project specific DQO).

12.4.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Reprepare and reanalyze the ICB.

12.5. Linear Dynamic Range

12.5.1. Following the initial instrument setup, the upper limit of the linear dynamic range for each analyte must be established for each wavelength utilized prior to initial calibration.

12.5.1.1. The upper range limit is established for each wavelength by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range.

12.5.1.2. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file.

12.5.2. Following the establishment of a valid initial calibration, the upper range limit must be checked every six months, and a new upper range limit should be determined whenever there is a significant change in instrument response.

12.5.2.1. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

12.5.3. The upper range limit is deemed valid if the %D for each analyte in a high-level check standard analyzed and quantitated against the calibration curve is ≤ 10%.

12.5.4. Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. Hence, non-linear second order curve may be used if the instrument allows it.

12.5.4.1. The effective range must be checked, and the correlation coefficient of the second order curve fit should be ≥ 0.995.

12.5.4.2. Non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

12.6. Daily Spectral Interference Check (ICS-AB and ICS-A)

12.6.1. Following the establishment of a valid initial calibration, the daily spectral interference check solutions must be analyzed daily prior to sample analysis and at the end of sequence.

12.6.1.1. The daily spectral interference check solutions are utilized to verify either the accuracy of the interelement correction factors if interelement corrections are applied, or the absence of interferences if interelement corrections are not applied.

12.6.2. The daily spectral interference check is deemed acceptable if the %D for each analyte is ≤ 20%.

12.6.3. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and reanalyze the ICS-AB and/or ICS-A.

12.6.4. All interelement spectral correction factors or multivariate correction matrices should be updated every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.7. Continuing Calibration Verification (CCV)

12.7.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

12.7.2. The initial calibration is deemed valid if the %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 10%.

12.7.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Effect corrective action and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, recalibrate.

12.8. Continuing Calibration Blank (CCB)

12.8.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > RL (or the limit specified in the project specific DQO).

12.8.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Reprepare and reanalyze the CCB.

12.9. ►Event Based Quality Control (LCS/LCSDs and MBs)

12.9.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)*** and, ***in some cases, a*** laboratory control sample duplicate (LCSD).

12.9.1.1. ***When requested by client, to meet project DQOs, or if insufficient sample volume is received for MS/MSD, a laboratory control sample duplicate (LCSD) is required.***

12.9.2. The acceptance criteria for LCS/LCSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. ***When an LCSD is done, the*** RPD is ≤ 20%.

12.9.2.2. All LCS/LCSD elements must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.9.2.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.9.2.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with

long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.9.2.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.9.2.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.9.2.7. If the problem was not related to the digestion process, then the LCS/LCSD and all associated sample digestates must be re-analyzed. If the failure was associated with the digestion process, then all associated samples must be re-processed and re-analyzed.

12.9.3. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.9.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.9.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgement should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.10. Matrix Based Quality Control (MS/MSDs and PDSs)

12.10.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.10.2. The acceptance criteria for MS/MSD elements are as follows:

12.10.2.1. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20%.

12.10.2.1.1. If historical data is available, then the lower and upper acceptance limits for %REC and %RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.10.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.10.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.10.3. ►Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the ***LCS or*** LCS/LCSD. Specifically, an acceptable ***LCS or*** LCS/LCSD usually supports matrix interference.

12.11. If the %REC or RPD of the MS/MSD and ***LCS or*** LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.12. Dilution Test

12.12.1. If the analyte concentration is sufficiently high, an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.12.2. If this criterion is not met, a physical or chemical interference effect shall be suspect. The MSA or the use of an internal standard may provide more accurate data.

12.13. Recovery Test (Post Digestion Spike Addition)

12.13.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution.

12.13.2. The acceptance criteria for PDS elements are as follows:

12.13.2.1. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

12.13.2.2. If the %REC of the PDS elements is not within the established acceptance limits, a matrix effect shall be suspect. The MSA or the use of an internal standard may provide more accurate data.

12.14. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Demonstration of Performance

13.1.1. Document the selection criteria for background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences.

13.1.2. Generate the data using the same instrument, operating conditions, and calibration routine to be used for sample analysis.

13.1.3. Keep the data on file and available for review.

13.2. Pipetter

13.2.1. ►Calibrate the pipetter according to the procedure outlined in the ***current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."***

13.3. Spectrometer Initial Calibration

13.3.1. Establish an acceptable one-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.3.2. After obtaining an acceptable one-point calibration curve and prior to processing sample or QC digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.3. and Section 12.4.

13.3.3. The initial one-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. ►***Sample Preparation***

14.1.1. ***Aqueous Sample Preparation – Dissolved Metals***

14.1.1.1. For the determination of dissolved metals in ground and surface waters, pipet an aliquot (of at least 20ml volume) of filtered, acid-preserved sample into a 50ml polypropylene centrifuge tube. Add an appropriate volume of (1:1) nitric acid to adjust the acid concentration of the sample aliquot to approximately 1% (v/v) nitric acid. The sample is now ready for analysis. Allowance for sample dilution must be made in the calculation.

14.1.1.1.1. If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be re-acidified, allowed to stand for a minimum of 2 days, and re-prepared.

14.1.2. ***Aqueous Sample Preparation – Total Recoverable Metals***

14.1.2.1. For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the procedure in Section 14.1.1.1.

14.1.2.2. For the determination total metals in all other aqueous samples or for pre-concentrating drinking water samples, perform the following:

14.1.2.2.1. For the determination of total metals in aqueous samples (other than drinking water with < 1 NTU turbidity), transfer a 50ml (or smaller) aliquot from a thoroughly mixed, acid-preserved sample to a digestion beaker.

14.1.2.2.2. Add 1ml (1:1) nitric acid and 0.50ml of (1:1) of hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on a hot plate for solution evaporation at a temperature of no higher than 85°C. Cover the beaker with an elevated watch glass which will raise the temperature of the evaporating solution to 95°C as well as protect the solution from the hood environment.

14.1.2.2.3. Reduce the volume of the sample aliquot to about 20ml by gentle heating at 85°C. Do not allow the solution to boil. This step should take approximately 2 hours for a 100ml sample aliquot.

14.1.2.2.4. Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. Slight boiling may occur, but vigorous boiling must be avoided to prevent the loss of the HCl-H_2O azeotrope.

14.1.2.2.5. Allow the beaker to cool. Quantitatively transfer the sample solution to a 50ml volumetric flask or similar container, make to volume with reagent grade water, and cover and mix.

14.1.2.2.6. Allow any undissolved material to settle overnight or centrifuge a portion of the prepared sample until clear. If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. If

filtering, care should be exercised to avoid potential contamination from filtration.

14.1.2.2.7. ***Prior to analysis, adjust the chloride concentration by pipetting 20ml of the prepared solution into a 50ml volumetric flask, dilute to volume with reagent grade water a thoroughly mix. If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the skimmer cones. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible post preparation.***

14.2. Instrument Setup

14.2.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 30 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.2.1.1. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality.

14.2.1.2. Deviations from instructions provided by the instrument manufacturer must be documented and approved by the Group Leader.

14.2.1.3. Use the following ICP-AES operating conditions as guidance.

Operating Condition	Aqueous Solution	Axial Plasma
Forward Power	1100–1450 watts	1100–1450 watts
Viewing Height	14–18 mm	
Argon Coolant Flow	15–19 L/min	15–19 L/min
Argon Nebulizer Flow	0.5–1.5 L/min	0.5–1.5 L/min
Sample Pumping Rate	1.0–3.0 mL/min	1.0–3.0 mL/min
Preflush Time	1 min	1 min
Measurement Time (Sequential Instrument)	~2 sec per wavelength peak	~2 sec per wavelength peak
Measurement Time (Simultaneous Instrument)	10 sec per sample	10 sec per sample

14.2.1.4. Repeatable interference correction factors can be achieved by adjusting the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively.

14.2.2. Refer to Appendix A for specific wavelengths. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference.

14.2.3. Optimize the plasma operating conditions prior to the use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, but only is required when first setting up a new instrument, or following a change in operating conditions. Apply the following procedure, or the instrument manufacturer's recommendations, to optimize the plasma operating conditions.

14.2.3.1. Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable (about 30 to 60 minutes of operation). While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

14.2.3.2. After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

14.2.3.3. Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical.

14.2.3.3.1. Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the judgment of the analyst. V, Cr, Cu, Li and Mn also have been used with success.

14.2.3.3.2. Collect intensity data at the wavelength peak for each analyte at 1-mm intervals from 14 to 18 mm above the load coil. This region of the plasma is referred to as the analytical zone.

14.2.3.3.3. Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the

elements analyzed or the highest intensity ratio for the least sensitive element.

14.2.3.3.4. Follow the instrument manufacturer's instructions for optimization in the axial mode.

14.2.4. The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits (IDLs).

14.2.5. If either the instrument operating conditions (such as incident power or nebulizer gas flow rate) are changed, or a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

14.2.6. After completing the initial optimization of operating conditions, and before analyzing samples, an interelement spectral interference correction routine to be used for sample analysis must be established and initially verified.

14.2.6.1. A general description of spectral interferences and the analytical requirements for background correction are discussed in Section 7.

14.2.6.2. The criterion for determining the presence of an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls beyond ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit.

14.2.6.3. Once established, the entire routine must be verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verifications of the routine should be kept on file.

14.2.7. Before daily calibration, and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

14.2.8. For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

14.2.9. Program the system to average at least duplicate readings on samples including the calibration standards, the calibration verification standards, the calibration blanks, the QC check samples and method blanks. Report the average.

14.2.9.1. If the %RSD for an analyte in a standard is > 5%, re-analyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-

preparation of the standard solution, and recalibrate, if necessary.

14.2.9.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, re-analyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.3. Establish sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

14.3.1. Establish method detection limits (MDLs) for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. Additional information regarding determination of detection limits is provided in SOP-T006.

14.3.2. Establish the upper limit of the linear dynamic range for each wavelength utilized (see Section 12.5.).

14.3.3. Verify that the instrument configuration and operating conditions satisfy the analytical requirements, and maintain quality control data confirming instrument performance and analytical results.

14.4. Establish a calibration curve to cover the appropriate concentration range (see Section 13.3.).

14.5. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A must be analyzed daily prior to sample analysis, and an ICS-AB must be analyzed at the end of sequence. The acceptance criteria are listed in Section 12.6.

14.5.1. If a failed ICS-AB/ICS-A is the first of the day, corrective action must be effected prior to analyzing any samples.

14.5.2. If not, effect corrective action and reanalyze all samples since the last acceptable ICS-AB.

14.6. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.7. and Section 12.8.

14.6.1. If a failed CCV/CCB is the first of the day, corrective action must be effected prior to analyzing any samples.

14.6.2. If not, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.7. Following digestion by one of the methods specified in Section 5.3., the digestates for the QC and actual environmental samples are received in autosampler vials. The autosampler vials are then loaded onto the ICP-AES sample tray.

14.7.1. Preliminary treatment of most matrices is necessary due to the complexity and variability of sample matrices.

14.7.2. All associated QC samples (MB/LCS/LCSD/MS/MSD) for the batch must undergo the same filtration and acidification procedures.

14.7.3. Groundwater samples which have been prefiltered and acidified will not need acid digestion.

14.7.4. Samples which are not digested must either use an internal standard or be matrix-matched with the standards.

14.8. ▶Sample vials are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard(s)
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Interference Check Solution AB (ICS-AB)
6) Interference Check Solution A (ICS-A)
7) Continuing Calibration Verification (CCV)
8) Continuing Calibration Blank (CCB)
9) Method Blank (MB)
10) Laboratory Control Samples (LCS)
11) Laboratory Control Sample Duplicates (LCSD), ***when applicable***
12) Samples (up to 10, including QC check samples and MBs)
13) Matrix Spike (MS)
14) Matrix Spike Duplicate (MSD)
15) Dilution Test Sample
16) Post Digestion Spike (PDS)
17) Ending ICS-AB (Optional)
18) Ending CCV
19) Ending CCB

14.8.1. Item 1: The CB is a vial of acidified reagent water used to establish the zero point of the initial calibration curve.

14.8.1.1. Additional calibration blanks may also be added elsewhere in the sequence to rinse the analytical system.

14.8.1.2. The rinse time is set to one minute. Rinse time may be reduced through a suitable demonstration.

14.8.2. Item 2: The initial calibration standard(s) are high-level calibration standard(s) used to establish the initial calibration curve.

14.8.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial one-point calibration. An acceptable ICV is required daily after initial calibration.

14.8.4. Item 4: The ICB is a vial of acidified reagent water used to monitor contamination. An acceptable ICB is required daily after initial calibration verification.

14.8.5. Items 5, 6, and 17: The ICS-AB and ICS-A are used to verify the accuracy of the interelement correction factors. An acceptable ICS-AB is required daily prior to sample analysis. An acceptable ICS-A is required daily prior to sample analysis.

14.8.6. Items 7 and 18: A CCV is used to verify the acceptance of the initial one-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

14.8.7. Items 8 and 19: A CCB is a vial of acidified reagent water used to monitor contamination. An acceptable CCB is required daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

14.8.8. Item 9: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.8.8.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of clean Teflon chips (or glass beads).

14.8.8.2. One MB is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.8.8.3. When samples that are leached/digested together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of acidified reagent water must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.8.9. Item 10: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.8.9.1. For aqueous samples, the LCS consists of the specified elements spiked into clean reagent water. For solid samples, the LCS consists of the specified elements spiked into clean Teflon chips (or glass beads).

14.8.9.2. One LCS is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.8.10. ►Item 11: The LCSD, ***when applicable,*** is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.8.11. Item 12: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.8.12. Item 13: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.8.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.8.12.2. One MS is required for every batch of 10 samples per matrix or portion thereof digested/leached concurrently.

14.8.13. Item 14: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.8.14. Item 15: The dilution test sample is prepared from the 1:5 dilution of an actual sample with the analyte concentration at a factor of 50 or greater above the IDL but < 90% of the upper limit of the linear dynamic range.

14.8.14.1. The purpose of the dilution test sample is to access physical or chemical interference effects.

14.8.14.2. For EPA Region 9 requirement, one dilution test sample is required daily for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.8.15. Item 16: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentrations of specific target analytes post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.8.15.1. The purpose of the PDS is to access matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.8.15.2. The number of PDS required is based upon client request or the project specific DQOs.

14.8.16. Rinse blanks may be added elsewhere in the sequence to rinse the analytical system.

14.9. Ensure that a sufficient amount of rinse blank is present in the rinse blank bottle, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.10. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.11. Initiate the sequence.

14.12. If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

14.13. Method of Standard Additions (MSA)

14.13.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a digested sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.13.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.10. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.13.3. Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then

plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix E. A linear regression program may be used to obtain the intercept concentration.

14.13.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.13.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.13.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.13.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

14.14. Data Interpretation

14.14.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between intensities in the sample digestate and the calibration standard(s).

14.14.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the intensity of an element can be determined.

14.14.1.2. Determine the concentration based on the initial calibration curve.

14.14.1.2.1. The data system is programmed to perform the calculation of concentration.

14.14.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{I_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the intensity readings for the target analyte.
I_{ave} = mean of the intensity readings for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The slope and intercept of a linear calibration curve are calculated as follows:

$$M = \frac{I_s - I_b}{C_s - C_b} \qquad B = \frac{C_s I_b - C_b I_s}{C_s - C_b}$$

where: M = slope of the calibration curve.
B = intercept of the calibration curve.
I_s = intensity of calibration standard at a specific wavelength.
I_b = intensity of calibration blank at a specific wavelength.
C_s = concentration of calibration standard.
C_b = concentration of calibration blank.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample digestate is calculated as follows:

$$C_x = \frac{I_x - B}{M}$$

where: C_x = concentration of target analyte in digestate in mg/L.
I_x = intensity of target analyte at a specific wavelength.
B = intercept of the calibration curve.
M = slope of the calibration curve.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in mg/L.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in g.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of solution A.
S_B = analytical signal (corrected for the blank) of solution B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.11. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.11.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and mg/kg (ppm) on a dry-weight basis for soil samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ►The acceptance criteria for LCS/LCSD elements are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. ***When an LCSD is done, the*** RPD is ≤ 20%. All LCS/LCSD elements must be within acceptance limits (see Section 12.9.2. for additional information).

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD ***(when applicable)*** is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.2. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.3. The acceptance criteria for MS/MSD elements are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20%.

18.3.1. Refer to Section 12.10.2.1.1. for acceptance criteria if historical data is available.

18.3.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

18.4.1. When the %REC of the PDS elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The PDS data shall be reported with the corresponding sample data.

18.4.2. If the %REC of the PDS elements are not within the established acceptance limits, the MSA results shall be reported with the corresponding sample data.

18.5. ►Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the ***LCS or*** LCS/LCSD. Specifically, an acceptable ***LCS or*** LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and mg/kg (ppm) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical

systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Method 200.7, USEPA, March 1983.

22.2. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 6010C, USEPA, Revision 3, November 2000.

22.3. *Metals by Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy (AES)*, EPA Method 200.7, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, March 2001.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Recommended Wavelengths and Estimated Instrumental Detection Limits.

23.2. Appendix B: Potential Interferences (Example), Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level.

23.3. Appendix C: Standard Solution Preparation.

23.4. Appendix D: Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples.

23.5. Appendix E: Standard Addition Plot (Example).

24. ►MODIFICATIONS

24.1. ***The following modifications from method EPA 200.7 are noted.***

24.1.1. ***None.***

25. ▸REVISION HISTORY

Revision	Description	Author	Effective Date
1.0	Section 5: Update method summary. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 24: Add Modifications. Section 25: Add Revision History.	K. Burney	06/17/13

Appendix A

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Calscience Environmental Laboratories, Inc.

Appendix A

Recommended Wavelengths and Estimated Instrumental Detection Limits (IDLs)

Element	Detection Wavelength [a] (nm)	Estimated IDL [b] (µg/L)
Aluminum (Al)	308.215	30
Antimony (Sb)	217.582	21
Arsenic (As)	193.696	35
Barium (Ba)	233.527	0.87
Beryllium (Be)	313.042	0.18
Boron (B)	249.677 × 2	3.8
Cadmium (Cd)	226.502	2.3
Calcium (Ca)	317.933	6.7
Chromium (Cr)	267.716	4.7
Cobalt (Co)	228.616	4.7
Copper (Cu)	324.752	3.6
Iron (Fe)	273.955	4.1
Lead (Pb)	220.353	28
Lithium (Li)	610.362	2.8
Magnesium (Mg)	279.077	20
Manganese (Mn)	257.610	0.93
Molybdenum (Mo)	202.031	5.3
Nickel (Ni)	231.604 × 2	10
Phosphorus (P)	213.617	51
Potassium (K)	766.490	See note [c]
Selenium (Se)	196.026	50
Silica (SiO2)	251.611	17
Silver (Ag)	328.068	4.7
Sodium (Na)	589.592	19
Strontium (Sr)	407.771	0.28
Thallium (Tl)	190.801	27
Tin (Sn)	189.927	17
Titanium (Ti)	336.121	5.0
Vanadium (V)	292.402	5.0
Zinc (Zn)	213.857 × 2	1.2

[a] The wavelengths listed (where ×2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 7.1.). In time, other elements may be added as more information becomes available and as required.

[b] The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c] Highly dependent on operating conditions and plasma position.

Appendix B

POTENTIAL INTERFERENCES (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix B

Potential Interferences (Example)

Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level [c]

Analyte		Wavelength (nm)	Interferant [ab] Al	Ca	Cr	Cu	Fe	Mg	Mn	Tl	V
Aluminum	Al	308.215	--	0.01926	0.01760	0.00290	--	0.00296	--	0.00470	0.63900
Antimony	Sb	206.836	--	--	1.50400	--	--	0.00116	--	--	--
Antimony	Sb	217.582	--	--	0.00910	--	--	0.00116	--	--	0.14900
Arsenic	As	188.979	--	--	--	0.00290	--	--	0.00440	0.00150	0.00040
Arsenic	As	193.696	--	0.00035	0.04780	--	--	--	--	--	--
Barium	Ba	233.527	0.00009	--	--	--	0.00403	0.00025	--	--	--
Beryllium	Be	313.042	--	--	0.00025	--	--	--	--	--	0.00650
Cadmium	Cd	226.502	--	--	--	--	0.00096	--	--	0.00005	0.00020
Calcium	Ca	317.933	0.00262	--	0.03450	0.00790	0.01350	0.02850	0.01330	0.00760	--
Chromium	Cr	267.716	0.00096	0.00009	--	0.02110	0.00186	0.00090	0.03080	0.00085	--
Cobalt	Co	228.616	0.00023	0.00001	--	0.00050	0.00166	0.00006	0.00045	0.00015	0.00050
Copper	Cu	324.752	0.00325	0.00229	--	--	--	0.00225	0.02680	0.04170	--
Iron	Fe	273.955	0.00617	--	0.01020	0.00660	--	0.00378	0.01140	0.00460	0.21900
Lead	Pb	220.353	--	--	--	0.00710	--	--	0.01530	0.00050	--
Magnesium	Mg	279.077	0.00066	0.00067	--	--	0.00049	--	--	0.00075	--
Manganese	Mn	257.610	--	0.00018	--	--	--	0.00041	--	0.00182	--
Molybdenum	Mo	202.031	0.00142	--	0.00625	0.00045	--	--	--	--	--
Nickel	Ni	231.604	0.00023	0.00002	0.00100	0.00010	0.00034	--	--	0.03940	0.00190
Phosphorus	P	213.617	--	--	--	0.87900	--	--	--	0.00430	0.01840
Potassium	K	766.490	--	--	--	--	--	0.00780	--	--	--
Selenium	Se	196.026	0.00667	--	--	0.00440	--	--	0.05840	--	0.00450
Silver	Ag	328.068	--	--	0.00040	0.00650	--	--	0.00045	--	--
Sodium	Na	589.592	0.09157	0.00801	0.10960	0.00580	--	0.13380	--	0.08005	--
Strontium	Sr	407.771	--	0.00258	0.00065	--	--	--	--	--	--
Thallium	Tl	190.801	0.00082	0.00378	0.04500	0.00445	0.00024	--	--	--	0.05500
Tin	Sn	189.927	0.00032	0.00301	--	0.00045	0.00059	--	0.00085	--	0.00165
Titanium	Ti	336.121	--	--	--	0.00015	0.00003	--	0.00010	0.00010	--
Vanadium	V	292.402	0.00011	--	--	--	--	0.00023	--	0.00025	--
Zinc	Zn	213.857	0.00041	0.00027	0.00285	0.05220	0.01660	0.00033	--	0.00100	--

[a] Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al - 200 mg/L		Mg - 200 mg/L	
Ca - 200 mg/L		Mn - 200 mg/L	
Cr - 1000 mg/L		Tl - 1000 mg/L	
Cu - 1000 mg/L		V - 1000 mg/L	
Fe - 200 mg/L			

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

Appendix C

STANDARD SOLUTION PREPARATION

Calscience Environmental Laboratories, Inc.

Appendix C

Standard Solution Preparation – Initial Calibration Standard

Initial Calibration Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	200 + 2000	60 + 7.5	27	1000
Antimony	Sb	200 + 1000	15 + 6	9	1000
Arsenic	As	500	15	7.5	1000
Barium	Ba	2000	7.5	15	1000
Beryllium	Be	50 + 50	15 + 7.5	1.125	1000
Boron	B	100 + 1000	15 + 6	7.5	1000
Cadmium	Cd	100	15	1.5	1000
Calcium	Ca	1000	60	60	1000
Chromium	Cr	20	60	1.2	1000
Cobalt	Co	500	7.5	3.75	1000
Copper	Cu	250	7.5	1.875	1000
Iron	Fe	1000	7.5	7.5	1000
Lead	Pb	500	15	7.5	1000
Lithium	Li	100	60	6	1000
Magnesium	Mg	1000	15	15	1000
Manganese	Mn	100	15	1.5	1000
Molybdenum	Mo	200	6	1.2	1000
Nickel	Ni	20	60	1.2	1000
Phosphorus	P	10000	1.2	12	1000
Potassium	K	400 + 10000	60 + 3	54	1000
Selenium	Se	200	15	3	1000
Silicon	Si	2000	6	12	1000
Silver	Ag	50	15	0.75	1000
Sodium	Na	200 + 10000	60 + 6	72	1000
Strontium	Sr	10	60	0.6	1000
Thallium	Tl	200	15	3	1000
Tin	Sn	1000	6	6	1000
Titanium	Ti	200	6	1.2	1000
Vanadium	V	500	7.5	3.75	1000
Zinc	Zn	100 + 10000	15 + 0.35	5	1000
Bismuth [b]	Bi	1000	0.02	2	10
Sulfur [b]	S	1000	0.02	2	10

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi and S standards are prepared separately.

Appendix C

Standard Solution Preparation – Initial Calibration Verification (ICV) Standard

Initial Calibration Verification (ICV) Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	200	4	4	200
Antimony	Sb	200	2	2	200
Arsenic	As	500	2	5	200
Barium	Ba	100	2	1	200
Beryllium	Be	50	2	0.5	200
Boron	B	500	1	2.5	200
Cadmium	Cd	150	2	1.5	200
Calcium	Ca	1000	4	20	200
Chromium	Cr	20	4	0.4	200
Cobalt	Co	100	2	1	200
Copper	Cu	100	2	1	200
Iron	Fe	10000	2	100	200
Lead	Pb	500	2	5	200
Lithium	Li	100	4	2	200
Magnesium	Mg	1000	2	10	200
Manganese	Mn	100	2	1	200
Molybdenum	Mo	100 + 300	2 + 1	2.5	200
Nickel	Ni	20	4	0.4	200
Phosphorus	P	1000	1	5	200
Potassium	K	400	4	8	200
Selenium	Se	200	2	2	200
Silicon	Si	230	1	1.15	200
Silver	Ag	50	2	0.5	200
Sodium	Na	200 + 10000	4 + 1	54	200
Strontium	Sr	10	4	0.2	200
Thallium	Tl	200	2	2	200
Tin	Sn	10000	0.05	2.5	200
Titanium	Ti	1000	1	5	200
Vanadium	V	100	2	1	200
Zinc	Zn	150	2	1.5	200
Bismuth [b]	Bi	1000	0.01	1	10
Sulfur [b]	S	1000	0.01	1	10

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi and S standards are prepared separately.

Appendix C

Standard Solution Preparation – Interference Check Standard AB (ICS-AB)

Interference Check Standard AB (ICS AB)					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	1200	10	24	500
Antimony	Sb	10000	0.05	1	500
Arsenic	As	1000	0.5	1	500
Barium	Ba	300	0.5	0.3	500
Beryllium	Be	100	0.5	0.1	500
Bismuth	Bi				
Boron	B	500	0.5	0.5	500
Cadmium	Cd	300	0.5	0.3	500
Calcium	Ca	6000	10	120	500
Chromium	Cr	300	0.5	0.3	500
Cobalt	Co	300	0.5	0.3	500
Copper	Cu	300	0.5	0.3	500
Iron	Fe	5000	10	100	500
Lead	Pb	1000	0.5	1	500
Lithium	Li				
Magnesium	Mg	3000	10	60	500
Manganese	Mn	200	0.5	0.2	500
Molybdenum	Mo	300	0.5	0.3	500
Nickel	Ni	300	0.5	0.3	500
Phosphorus	P				
Potassium	K	20000	0.5	20	500
Selenium	Se	500	0.5	0.5	500
Silicon	Si	230	0.5	0.23	500
Silver	Ag	300	0.5	0.3	500
Sodium	Na	1000	10	20	500
Strontium	Sr				
Thallium	Tl	1000	0.5	1	500
Tin	Sn				
Titanium	Ti	1000	0.5	1	500
Vanadium	V	300	0.5	0.3	500
Zinc	Zn	300	0.5	0.3	500

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Standard Solution Preparation – Interference Check Standard A (ICS-A)

Interference Check Standard A (ICS A)					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	1200	10	24	500
Calcium	Ca	6000	10	120	500
Iron	Fe	5000	10	100	500
Magnesium	Mg	3000	10	60	500
Sodium	Na	1000	10	20	500

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Standard Solution Preparation – Internal Standard

Internal Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Holmium	Ho	1000	0.5	5	100
Terbium	Tb	1000	0.5	5	100
Yttrium	Y	1000	0.5	5	100

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Standard Solution Preparation – Spike Standards

Spike Standards 1 & 2					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	10000	10	100	1000
Antimony	Sb	10000	10	100	1000
Arsenic	As	10000	10	100	1000
Barium	Ba	10000	10	100	1000
Beryllium	Be	10000	10	100	1000
Boron	B	10000	10	100	1000
Cadmium	Cd	10000	10	100	1000
Calcium	Ca	10000	10	100	1000
Chromium	Cr	10000	10	100	1000
Cobalt	Co	10000	10	100	1000
Copper	Cu	10000	10	100	1000
Iron	Fe	10000	10	100	1000
Lead	Pb	5000 [b]	20	100	1000
Magnesium	Mg	10000	10	100	1000
Manganese	Mn	10000	10	100	1000
Molybdenum	Mo	10000	10	100	1000
Nickel	Ni	10000	10	100	1000
Phosphorus	P	10000	10	100	1000
Potassium	K	10000	100	1000	1000
Selenium	Se	10000	10	100	1000
Silicon	Si	10000	10	100	1000
Silver	Ag	10000	5	50	1000
Sodium	Na	10000	100	1000	1000
Strontium	Sr	10000	10	100	1000
Thallium	Tl	10000	10	100	1000
Tin	Sn	10000	10	100	1000
Titanium	Ti	10000	10	100	1000
Vanadium	V	10000	10	100	1000
Zinc	Zn	10000	10	100	1000
Bismuth [c]	Bi	1000	0.05	0.5	100
Sulfur [c]	S	1000	0.05	0.5	100
Lithium [c]	Li	10000	0.005	0.5	100

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] The 5000-ppm Pb spike solution is prepared from the 10000-ppm pre-certified stock standard solution.

[c] Bi ,S, and Li are spiked directly into 50-mL sample.

Appendix D

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Calscience Environmental Laboratories, Inc.

Appendix D

Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples

Measurement		Digestion Volume (mL) [a, c]	Collection Volume (mL) [a, c]	Treatment/Preservative Holding Time [b]
Inorganic Analytes (except hexavalent chromium and mercury):				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 6 months
	Dissolved	50	250	Filter on site HNO_3 to pH < 2 6 months
	Suspended	50	250	Filter on site 6 months
Solid				
	Total	2 g	4 oz	6 months
Hexavalent Chromium:				
Aqueous		50	250	24 hours Store at 4 ± 2°C until analyzed
Solid		2.5 g	4 oz	1 month to extraction 4 days after extraction Store at 4 ± 2°C until analyzed
Mercury:				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 28 days
	Dissolved	50	250	Filter HNO_3 to pH < 2 28 days
Solid				
	Total	0.2 g	4 oz	28 days Store at 4 ± 2°C until analyzed

[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

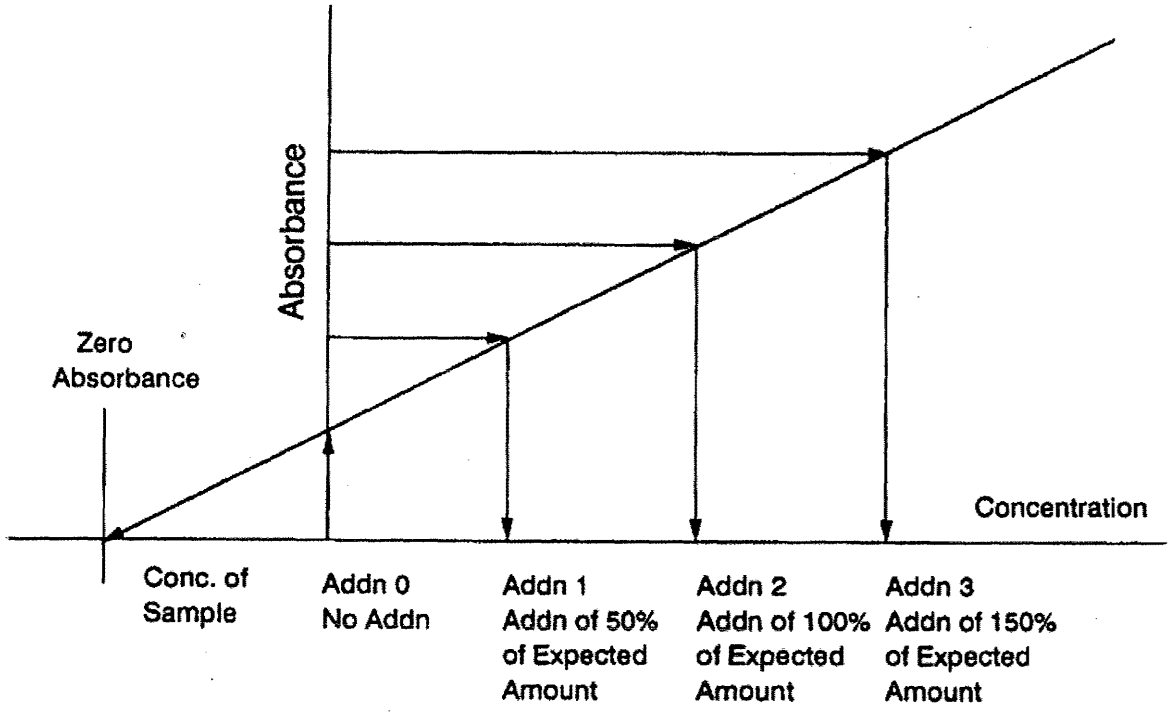
Appendix E

STANDARD ADDITION PLOT (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix E

Standard Addition Plot (Example)



Title : **EPA METHOD 218.6, DETERMINATION OF DISSOLVED HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY**

Document No. : SOP-M741
Revision No. : 2.0
Supersedes : 1.3

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PROPRIETARY INFORMATION STATEMENT

Revision 2.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 09/22/15
MANAGEMENT **DATE**

_____ 09-22-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 218.6, Determination of Dissolved Hexavalent Chromium by Ion Chromatography.

2. APPLICABLE MATRICES

2.1. Method 218.6 is applicable for the determination of dissolved hexavalent chromium in drinking water, ground water and industrial wastewater effluents.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The approximate detection limit in drinking water samples is 0.2 µg/L. ***Higher limits, 1.0 µg/L, may be seen with 'unfinished' aqueous samples or should the low level RL not be required.***

3.2. The RLs will be proportionally higher for samples which require dilution ***due to concentration and/or other interference.***

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography (IC) and skillful in the interpretation of chromatographic data.

5. METHOD SUMMARY

5.1. An aqueous sample is filtered through a 0.45-µm filter and the filtrate is adjusted to a pH = 9.0-9.5 with a buffer solution.

5.2. ►A measured volume of the sample (***1000*** µL) is introduced into the ion chromatograph. The sample is passed through a guard column to remove organic materials and, subsequently, is passed through an analytical column to separate hexavalent chromium. Hexavalent chromium undergoes post-column derivatization with 1,5-diphenylcarbazide to form a highly-colored complex which is detected at 530 nm.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.2.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.2.2. A filtration batch is composed of one to 20 aqueous environmental samples filtered at the same time using the same batch of filters and syringes. The associated quality control (MB and LCS, MS, etc.) must be prepared at the same time and be treated in the same manner as the field samples. The filtration procedure must be documented so as to allow for the traceability and linking of the initial analyses, dilution analyses, and QC analyses together.

6.2.2.1. Filtrates, if maintained in appropriate condition (i.e., covered container) and at the appropriate temperature (i.e., refrigerated if not in use) may be used for both initial and dilution analyses, as applicable to the sample and any target analytes present within.

6.2.2.2. In the above case, filtration batches may be associated with the same set of QC samples (MB and LCS, MS, etc.) even if analyzed on different days.

6.2.2.3. If a new filtered aliquot must be generated for dilution analysis, all applicable QC (MB, LCS/LCSD or LCS/MS/MSD) must also be prepared and a new batch created.

6.2.3. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.3. Continuing Calibration Verification (CCV): Also known as the Instrument Performance Check (IPC) Sample.

6.4. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised.

6.5. Initial Calibration Verification (ICV): Also known as the Quality Control Sample (QCS). An uncontaminated sample matrix spiked with known concentrations of analytes from a source independent from the calibration standards.

6.6. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.7. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an

independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.8. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.9. Method Blank: A sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.10. ***Refer to the current version of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. ►INTERFERENCES

7.1. ***Samples containing high levels of potassium permanganate may interfere with the accurate quantitation of hexavalent chromium and may lead to biased high results. This interference appears to be due to a reaction of permanganate with the post-column reagent that gives a colored species with much less absorbance at 530-nm than either permanganate itself or the complex of chromium species with the post-column reagent.***

7.1.1. ***Samples containing high levels of permanganate may be effectively treated with ascorbic acid. However, the amount of ascorbic acid should not exceed more than 1000mg/L due to potential negative effects on the instrumentation.***

7.2. ***Samples containing high levels of organic materials and/or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). In addition, reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. However, at a pH of 6.5 or greater, CrO_4^{2-}, which is less reactive than the $HCrO_4^-$, is the predominant species.***

7.3. ***Samples containing high levels of anionic species such as sulfate and chloride can result in loss of Cr(VI) due to column overload. Poor recoveries from spiked samples and tailing peaks are typical manifestations of column overload.***

7.4. ***Contamination may come from trace amounts of Cr which is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess for potential Cr(VI) contamination. Contamination may also be a result of improperly cleaned glassware or contact with caustic or acidic reagents of samples with stainless steel or pigmented material.***

7.5. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.6. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated chromatographic baseline.

7.7. Samples that contain particles larger than 0.45-µm and reagent solutions that contain particles larger than 0.20-µm require filtration to prevent damage to instrument columns and flow systems.

8. ►SAFETY

8.1. ***Hexavalent chromium is toxic and is a suspected human carcinogen where exposure may result in lung or other forms of cancer. For this reason, the inorganic salt must be handled with extreme care when weighing out standards or when handling the aqueous form, whether standards or samples.***

8.2. ***The salt form should be handled in a hood to avoid accidental exposure through inhalation and/or ingestion. If inhaled, remove to fresh air and seek medical attention as needed. If ingested, do not induce vomiting and seek immediate medical attention.***

8.3. ***Skin exposure to the salt or liquid form may cause skin irritation and/or a more intense allergic reaction resulting in a rash. Thoroughly wash all exposed areas with soap and water and rinse thoroughly. Seek medical attention should the rash intensify.***

8.4. ***Be sure to wear proper eye protection at all times and remove and properly separate soiled lab coats or other contaminated clothing in the event of splashing or spills.***

8.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling samples and chemicals.

8.6. Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Ion Chromatograph

9.1.1. Dionex DX-500, DX-600, ICS-3000 or ICS-5000 Ion Chromatograph configured with a post-column reagent delivery module and an autosampler.

9.1.2. Eluent Pump: capable of withstanding a minimum backpressure of 2000 psi and of delivering a constant flow in the range of 0.3–5 mL/minute.

9.1.3. Sample Loop, 1000 µL (250 µL for standard reporting levels).

9.1.3.1. The flow rate, after the absorbance detector, is set at approximately 0.35 mL/min for the low-level analysis and between 1.0 and 2.0 mL/min for the regular level analysis.

9.1.4. Detector: Absorbance.

9.1.5. Analytical Column: Dionex IonPac AS7, 4-mm or equivalent for regular level reporting and 2-mm for low-level reporting.

9.1.6. Guard Column: Dionex IonPac NG1, 4-mm or equivalent for regular level reporting and 2-mm for low-level reporting.

9.2. Instrument Software

9.2.1. ***Requires a PC based data system or equivalent.***

9.2.2. Dionex Chromeleon version 6.80 or Peaknet version 6.4, or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. ***Preventive maintenance should be performed at least annually and should involve the following:***

9.3.1.1. ***Rebuilding the injection valve and the auxiliary valves.***

9.3.1.2. ***Replacing the pump check valves.***

9.3.1.3. ***Replacing the pump piston rinse seals and piston seals.***

9.3.1.4. ***Replacing the waste valve and priming valve O-rings.***

9.3.1.5. ***Replacing the end-line filter.***

9.3.2. Additional information can be found in the user manual or operating guide for the specific Dionex instrument.

9.3.3. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.5. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.6. Ultra high purity Helium.

9.7. Class "A" Volumetric flasks: 10, 100, and 1000 mL, or other volumes as needed.

9.8. Calibrated Pipetters: 0.1 and 1 mL, or other volumes as needed.

9.9. Pipette tips, variable sizes.

9.10. Magnetic stirrer and stir bars, Teflon coated, for standard preparation.

9.11. pH meter, capable of an accuracy reading of ± 0.03 pH units.

9.12. pH paper, narrow-range, pHydrion Controls 9.0 to 10.0, or equivalent.

9.13. Transfer pipettes, disposable.

9.14. Erlenmeyer flasks: 125 mL or other volumes as needed.

9.15. Sample Filtration Device

9.15.1. Disposable syringes, 10-mL, luer-lock.

9.15.2. Syringe filter disks, 0.45-µm, luer-lock.

9.15.3. Syringe filter disks, 0.2-µm, luer-lock.

9.16. Beakers and graduated cylinders: 50, 100 and 500 mL or other volumes as needed.

9.17. Graduated cylinders, 50, 100, 500 mL, or other volumes as needed.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent Water: Ultrapure water having conductivity ≥ 18MΩ.

10.1.2. Ammonium sulfate, $(NH_4)_2SO_4$, ACS grade or equivalent.

10.1.3. Ammonium hydroxide, NH_4OH, 28-30%, ACS grade or equivalent.

10.1.4. Eluent Solution: 250-mM $(NH_4)_2SO_4$ and 100-mM NH_4OH.

10.1.4.1. In a 1000mL volumetric flask, dissolve 33.00 ± 0.33 g of ammonium sulfate in 500-mL reagent water, and add 6.5-mL ammonium hydroxide. Dilute to final volume (1000 mL) with reagent water and degas with helium for 10 minutes.

10.1.5. 1,5-diphenylcarbizide, $C_{13}H_{14}N_4O$, ACS grade or equivalent.

10.1.6. Methanol, CH_3OH, HPLC grade or equivalent.

10.1.7. Sulfuric acid, H_2SO_4, concentrated, ACS grade or equivalent.

10.1.8. Post column reagent:

10.1.8.1. In a 1000-mL volumetric flask, dissolve 0.5000 ± 0.005 g of 1,5-diphenylcarbazide in 100-mL HPLC grade methanol. In a 1000-mL beaker or flask, add 28 mL of 98% sulfuric acid to 500-mL reagent water, mix, and degas with helium for 10 minutes.

10.1.8.2. Once degassing is completed, add the H_2SO_4 solution to the diphenylcarbazide solution and then dilute to final volume (1000 mL) with reagent water. The post column reagent must be prepared fresh every 3 days, if not sooner, due to stability issues.

10.1.9. Buffer solution:

10.1.9.1. In a 100-mL volumetric flask, dissolve 3.30 ± 0.03 g of ammonium sulfate in 75-mL reagent water and add 6.5-mL ammonium hydroxide. Dilute to final volume (100 mL) with reagent water.

10.1.10. Potassium dichromate, $K_2Cr_2O_7$, ACS grade or equivalent.

10.1.11. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. ***Stock Standard: Inorganic Salts***

10.2.1.1. ***Potassium dichromate ($K_2Cr_2O_7$): Fisher # P188-500 or J.T. Baker # 3090-01, or equivalent.***

10.2.1.2. ***Intermediate standards are prepared by first drying the inorganic salts for 1 hour in a drying oven at 103−105°C. After drying, cool to ambient temperature in a desiccator. Inorganic salts should be stored in a desiccator when not in use.***

10.2.2. ***Intermediate Standard: 1000-ppm Hexavalent Chromium***

10.2.2.1. ***To make the 1000-ppm intermediate solution, weigh 0.2829 ± 0.0028 g of potassium dichromate ($K_2Cr_2O_7$) into a 100-mL volumetric flask and dilute to volume with reagent water. Stopper the flask and invert three times. Store the intermediate solution under refrigeration when not in use.***

10.2.2.1.1. ***If the salts won't go readily into solution, place a small stir bar into the flask, stopper, and place on a magnetic stirrer until the salts have dissolved. Add the stir bar after bringing to volume.***

10.2.2.2. ***Prepare the 1000-ppm intermediate standard fresh every six months.***

10.2.2.2.1. ***The expiration date is 6 months from preparation date unless the manufacturer's date on the inorganic salt is less than this time period; if so, then the manufacturer's date will take precedence for the intermediate and all working solutions.***

10.2.2.3. ***Repeat this same process for the second source standard.***

10.2.3. ***Working standard: 10-ppm Hexavalent Chromium***

10.2.3.1. ***Prepare a 10-ppm (10000-ppb) working standard by diluting 0.50 mL of the 1000-ppm intermediate standard to a final volume of 50 mL with reagent water.***

10.2.3.2. ***Alternatively, the working standard is prepared gravimetrically by weighing exactly 100.0 g of reagent water into a specimen cup. Quickly remove exactly 1.0 mL of the water using a calibrated pipetter. Then add exactly 1.0 mL***

of the 1000-ppm intermediate standard to the specimen cup using a calibrated pipetter.

10.2.3.3. ***Cap tightly and invert 3 times to mix. This will result in a 10-ppm working standard.***

10.2.3.3.1. ***This expiration date on the 10ppm working solution is 6 months, earlier if the manufacturer's date is less.***

10.2.3.3.2. ***Prepare calibration, verification, and spiking standards from this working standard using calibrated pipetters and serial dilution, as noted below.***

10.2.3.4. ***Repeat this same process for the second source standard.***

10.2.3.5. ***Initial Calibration Standards:***

10.2.3.5.1. ***Initial Calibration standards are prepared by diluting the appropriate amounts of the working standard with reagent water and buffer solution.***

Standard Concentration (ppb)	Final Volume (mL)	Initial Concentration (ppb)	Initial Volume (mL)	Buffer Volume (mL)
100	100	10000	1.0	1.0
75	10	100	7.5	0.10
50	50		25	0.50
25	10		2.5	0.10
10	100		10	1.0
5.0	10		0.50	0.10
1.0			0.10	
0.20			0.020	
0.050		1.0	0.50	
0.020			0.20	

10.2.3.6. ***Calibration standards must be prepared fresh on day of use.***

10.2.3.7. ***Initial and Continuing Calibration Verification (ICV/CCV) solutions and Spiking Solution.***

10.2.3.7.1. ***Prepare the ICV solution by diluting 0.50 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water. This same solution will be used as the spiking solution for the LCS and MS/MSD.***

10.2.3.7.2. ***Prepare CCV solutions by diluting 0.50 mL of the 10-ppm working standard and 1.0 mL of***

buffer to a final volume of 100 mL with reagent water.

10.2.3.7.3. ***Prepare ICV solutions for low-level analysis by diluting 0.10 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water.***

10.2.3.7.4. ***Prepare CCV solutions for low-level analysis by diluting 0.10 mL of the 10-ppm working standard and 1.0 L of buffer to a final volume of 100 mL with reagent water.***

10.2.3.7.5. ***Standards may be prepared in volumetric flasks or via the gravimetric approach.***

10.2.3.8. ***Second-source standards will be used to prepare the Initial Calibration Verification (ICV), Laboratory Control Sample (LCS), and Matrix Spike (MS) solutions.***

10.2.3.9. ***10-ppm Spiking Solution***

10.2.3.9.1. ***Prepare the spiking solution by diluting 0.50 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water. This solution will be used to spike the LCS and MS/MSD.***

10.2.3.9.2. ***Prepare LCS solutions for low-level analysis by diluting 0.10 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water.***

10.2.3.9.3. ***Standards may be prepared in volumetric flasks or via the gravimetric approach.***

10.2.4. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.3. ***Solutions may be prepared in final volumes other than those noted, provided that correct ratios of all components are maintained.***

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL HDPE containers with Teflon-lined lids.

11.1.1. Per 40CFR, Part 136.3, Table II, footnote 20, the analytical holding time for wastewaters may be extended to 28 days if both a filtration step and a buffering step, to adjust the pH to 9.3 – 9.7, are performed within the first 24 hours from collection.

11.1.1.1. Upon client request, containers with buffer at a ratio of 1mL buffer per 100mL sample will be provided, along with an

additional supply of buffer solution. For traceability, the containers will be labeled with the ID number of the buffer solution.

11.1.1.1.1. Client must field filter each sample and collect it in a buffered container, then measure pH and record it on the Chain of Custody (CoC).

11.1.1.1.2. If the pH is not within the required range (9.3 – 9.7), client must add additional buffer immediately and re-measure pH, then record the volume of buffer added and the final pH on the CoC.

11.1.1.2. The CoC must clearly indicate that the containers for Cr^{+6} analysis have been buffered, and must include:

11.1.1.2.1. Field pH of each sample.

11.1.1.2.2. Volume of additional buffer used, and final pH, if applicable.

11.1.1.2.3. Instructions to check the pH upon receipt and adjust preservation as needed.

11.1.1.3. Upon receipt at the laboratory, the pH will be checked and adjusted further (if needed), and the final pH of the sample will be recorded in the pH logbook.

11.2. Samples should be maintained in a chilled state, 0-6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions.

11.3. Bring to ambient temperature prior to analysis.

11.4. Unbuffered aqueous samples must be analyzed within 24 hours of collection.

11.5. ►Properly buffered samples ***(to pH 9.3-9.7 within 24 hours)*** must be analyzed within 28 days of collection.

12. ►QUALITY CONTROL

12.1. ***Method Detection Limit Study:***

12.1.1. ***A valid MDL study must be performed prior to sample processing.***

12.1.2. ***The MDL must be verified initially, immediately following the MDL study and then again annually for NELAC. A quarterly DL verification must be performed for DOD work.***

12.1.2.1. ***In order to meet the verification criteria for NELAC and DOD, the verification samples should be spiked at a level 2-4x the actual MDL.***

12.1.3. ***The MDL must be repeated for any major changes to the instrumentation or when the column is replaced, if an MDL verification standard does not support the current MDL (loss of sensitivity).***

12.1.4. ***Refer to the current version of SOP-T006 for further information regarding the MDL/DL process.***

12.2. ***Initial Demonstration of Capability***

12.2.1. ***All analysts must participate in an initial demonstration of capability (IDOC) and successfully meet the requirements in order to process and report data on their own. These requirements must be met at a minimum of annually with the processing of a continuing demonstration of capability (CDOC).***

12.2.2. ***An IDOC consists of preparing/analyzing four replicate LCS samples.***

12.2.3. ***Analysts without a current IDOC or CDOC are not allowed to report data without direct oversight by a senior chemist or group leader.***

12.3. ***DL/LOD/LOQ Study for DOD Samples***

12.3.1. ***A valid Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ) study shall be performed prior to the analysis of DOD samples. Please refer to section 7.6 and to the current version of SOP T006, Appendix A for further information on the processing of the DL/LOD/LOQ study.***

12.4. QC Overview

QC Element	Frequency	Acceptance Criteria	Corrective Action Section
Multipoint ICAL (Minimum 5 Points)	Initially, prior to sample or QC analysis. As needed thereafter, and at least annually.	r = 0.999 or r^2 = 0.998	12.5.1.
ICV / CCV	ICV: Immediately following the ICAL standards. CCV: Daily/Opening, bracketing every 10 samples, and at the end of the sequence.	ICV %D: ± 5% CCV %D: ± 5%	12.5.2. / 12.5.4.
ICB / CCB	ICB: Immediately following the ICV. CCB: Immediately following the CCV, throughout the sequence.	ICB: ND ≤ MDL/DL CCB: ND ≤ MDL/DL	12.5.3. / 12.5.5.
RT Window	Establish initially and then update daily with first CCV / midpoint ICAL standard.	Analyte retention time must fall within defined window.	12.6.
Method Blank	1 per batch of 20 samples	ND < ½ RL or < ½ LOQ (DOD)	12.7.

QC Element	Frequency	Acceptance Criteria	Corrective Action Section
LCS	1 per batch of 20 samples (LCS/LCSD if insufficient volume for MS/MSD)	%REC: 95% - 107% RPD: 20% (LCS/LCSD)	12.8.
MS / MSD	1 pair per batch of 20 samples	%REC: 85% - 121% RPD: 25%	12.9.

12.5. Instrument Calibration

12.5.1. Multi-point Initial Calibration (ICAL):

12.5.1.1. The instrument must be properly calibrated prior to the processing of sample extracts. This is done by analyzing a calibration blank and then 6 sequential points in order of increasing concentration (8 points if low-level analysis is performed).

12.5.1.2. The initial calibration is assumed to be valid with a correlation coefficient (r) of 0.999 or greater, or a coefficient of determination (r^2) of 0.998 or greater. This criterion is applicable to all samples and projects including DOD work.

12.5.1.2.1. ***The ICAL is routinely evaluated using r^2 (coefficient of determination) in both the Dionex data system and in LIMS, thus at least 6 sequential points must be used in the curve.***

12.5.1.3. If this criterion is not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and re-calibrate.

12.5.2. Initial Calibration Verification (ICV):

12.5.2.1. Following the analysis of the initial calibration standards an initial calibration verification (ICV) standard must be analyzed.

12.5.2.2. The ICV is deemed acceptable if the %D is ≤ 5%. This criterion is applicable to all samples and projects including DOD work.

12.5.2.2.1. If this criterion is not met, the initial calibration is deemed unacceptable for sample analysis to begin.

12.5.2.2.2. Effect corrective action and reprepare/reanalyze a new ICV aliquot to confirm the recovery. If the ICV still fails to meet acceptance criteria, recalibrate the instrument. The second ICV analysis must be performed prior to the analysis of any samples or QC elements.

12.5.2.2.2.1. If samples or QC have been analyzed (say, a sequence was run

overnight), then the instrument must be recalibrated and validated with a passing ICV and all samples reanalyzed against the passing ICAL.

12.5.3. Initial Calibration Blank (ICB):

12.5.3.1. Immediately following the ICV, analyze the ICB.

12.5.3.2. Prepare ICBs by diluting 1.0mL of buffer to a final volume of 100mL with reagent water.

12.5.3.3. The ICB is deemed acceptable if it is ≤ MDL/DL where the MDL/DL represents the current MDL for the target analyte.

12.5.4. Continuing Calibration Verification (CCV)

12.5.4.1. Following establishment of a valid initial calibration, a continuing calibration verification (CCV) standard must be analyzed at the beginning of a sequence, bracketing every 10 samples throughout the sequence, and then at the end of the sequence.

12.5.4.2. The CCV is deemed acceptable if the %D is ≤ 5%. This criterion is applicable to all samples and projects including DOD work.

12.5.4.2.1. If the %D is ≤ 5%, then the calibration is assumed to still be valid and sample analysis may continue.

12.5.4.2.2. If this criterion is not met, the CCV is deemed unacceptable. Reprepare and/or reanalyze the CCV one time. If the %D criterion remains unacceptable, effect corrective action, recalibrate the instrument, and reanalyze all samples analyzed since the last acceptable CCV.

12.5.5. Continuing Calibration Blank (CCB)

12.5.5.1. Prepare CCBs by diluting 1.0mL of buffer to a final volume of 100mL with reagent water.

12.5.5.2. A continuing calibration blank (CCB) must be analyzed following each CCV throughout the analytical sequence.

12.5.5.3. The acceptance criterion for the CCBs is ≤ MDL/DL (when reporting to the MDL) where the MDL/DL represents the current method detection limit for the target analyte. If reporting to the RL or LOQ, the CCB is deemed acceptable if ND at or below ½ the RL or LOQ (DOD work).

12.5.5.4. If the CCB fails (its result greater than the MDL/DL when reporting to the MDL or ≥ ½ RL/LOQ when reporting to the RL/LOQ) it should be immediately reanalyzed to confirm the detection. If it fails again, the analytical system is considered

out of control, and the cause must be determined and corrected prior to the analysis of samples.

12.5.5.4.1. This would tend to indicate instrument contamination and may require that you change guard columns, sample tubing, or even the analytical column. Perform maintenance as needed to correct the contamination issue and then reanalyze all samples that are positive for hexavalent chromium.

12.6. ***Retention Time Window***

12.6.1. ***Prior to the analysis of samples, establish the retention time window for hexavalent chromium Cr(VI) as per the procedure outlined in SOP-T020.***

12.6.2. ***Daily retention time windows are based upon the retention time of the analyte in the CCV ± three times the mean standard deviation and are to be updated in the instrument method/data system after the analysis of the opening CCV (midpoint of the ICAL, if analyzed) and prior to further data processing.***

12.6.3. ***All subsequent standards in an analysis sequence must fall within the daily retention time window established by the first CCV. If not, identify the reason for the drift/shift, effect corrective action, and reanalyze any samples that are associated with/bracketed by those standards.***

12.6.4. ***Occasionally, sample matrix may create a shift in the retention time window for a sample that may also impact the following CCV. In this case, reanalyze the sample to confirm that matrix effects are the reason for the shift and not the instrument. In addition, post spiking the sample to confirm that the peak is in fact hexavalent chromium may be warranted in order to properly report the analyte in a sample.***

12.6.4.1. ***To post spike, estimate the concentration in the sample and then spike at a similar level. Reanalyze the post-spiked sample aliquot. If the peak is truly Cr(VI), it should essentially double in height and area. If the peak appears to be split at a value greater than 20% resolution, and/or two peaks are clearly present, then it has not been confirmed.***

12.6.5. ***Retention time windows shall be recalculated whenever a new column is installed.***

12.7. Method Blank (MB):

12.7.1. For aqueous samples, the MB consists of reagent water pH adjusted to 9.0–9.5 with buffer solution. For solid samples, the MB consists of washed sea sand.

12.7.2. The method blank is used to verify that the systems and processes are not contributing contamination to the preparation and/or analytical process. A method blank is prepared at a minimum rate of one for every 20 samples of the same matrix.

12.7.3. The concentration of hexavalent chromium in the method blank must be less than the reporting limit (RL) or ½ the LOQ if DOD. If the concentration of the target analyte exceeds its RL (½ LOQ), the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.7.3.1. If hexavalent chromium is found in the MB, but not in the associated samples, report the sample and MB without qualification. Address the positive MB and the lack of impact on data quality in the narrative. Projects or programs may require correction action for a positive MB. This would consist of reanalysis of the associated samples.

12.7.3.2. If hexavalent chromium is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination and reprepare and reanalyze the samples.

12.7.3.2.1. Due to the short holding time for aqueous Cr(VI), reanalyzing the sample(s) within HT may not be feasible.

12.7.3.2.2. If the result in the sample(s) is greater than 10x the MB level, chances are the impact on data quality will be minimal; however, reanalyze as soon as possible to confirm the concentration. Report the first set of data, flag the results with a "B", and narrate the event.

12.7.4. Sample results <u>will not</u> be corrected for any values found in the associated method blank.

12.8. Laboratory Control Sample (LCS):

12.8.1. For aqueous samples, the LCS consists of the target analyte spiked into reagent water with buffer solution. For solid samples, the LCS consists of the target analyte spiked into washed sea sand. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control by measuring the percent recovery (%REC) of the spiked compound. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

12.8.1.1. One LCS is required for every batch of 20 samples per matrix or portion thereof.

12.8.1.2. When requested by client, to meet project DQOs, or if insufficient sample volume is received for an MS/MSD, a laboratory control sample duplicate (LCSD) is required.

12.8.1.3. The LCSD, when applicable, is handled identically to the LCS including frequency (every 20 samples). In addition to assessing accuracy, the LCS in combination with the LCSD can be used to assess the precision of the analytical process expressed as relative percent difference (RPD).

12.8.2. The acceptance criteria for Cr(VI) in the LCS is 95-107% recovery. If an LCSD is also analyzed, the %RPD is 20%. The criteria apply to routine and DOD project samples.

12.8.2.1. The LCS (LCS/LCSD) must be within acceptance criteria for the batch to be valid. If not, the samples must be reanalyzed (reprepared and reanalyzed if solid samples) with an acceptable LCS (LCS/LCSD) with the following exceptions:

12.8.2.1.1. If the LCS fails high and the associated samples are ND, the data may be reported with narration.

12.8.2.1.2. If the samples are outside of holding time, and/or there is insufficient sample mass/volume to reprepare, report the original data, flag as needed, and address the impact to data quality in the case narrative.

12.8.2.2. If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported and corrective action taken for recoveries and/or RPDs that are outside acceptance criteria.

12.8.2.3. The same LCS recovery criterion applies to the LCSD with the following exceptions:

12.8.2.3.1. If the LCS passes but the LCSD fails low (or vice versa); the batch is not acceptable and all affected samples should be reanalyzed.

12.8.2.3.2. If the RPD is outside criteria but the recoveries are within criteria in both the LCS and LCSD and all associated samples are ND, the data may be reported with narration.

12.8.2.3.3. If one of the LCSs is within criteria and the other is bias high, and the associated samples are all ND, the data may be reported with narration if there is insufficient holding time remaining. Otherwise, reanalyze with a passing LCS/LCSD.

12.9. Matrix Spike / Matrix Spike Duplicate (MS/MSD):

12.9.1. The MS is the actual matrix spiked with a known concentration of the target analyte. The purpose of a MS is to assess the effect of a sample matrix on

the recovery of target analyte. The measurement is expressed as percent recovery (%REC) of the spiked compound. The sample which is spiked for the MS is processed concurrently with the associated samples. The MSD is handled identically to the MS. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The precision is expressed as relative percent difference (RPD).

12.9.1.1. One MS/MSD pair is required for every batch of 20 samples per matrix or portion thereof.

12.9.2. The acceptance criteria for Cr(VI) in the MS/MSD is 85-121%, and the %RPD is 25%. The criteria apply to routine and DOD project samples.

12.9.2.1. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance.

12.9.2.2. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

12.9.2.3. If the %REC or RPD of the MS/MSD and LCS are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and reanalyzed.

12.10. Additional information about internal quality control checks is provided in SOP-T020.

13. ▶CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2mg, 1g, and 100g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Top Loading Balance

13.2.1. Calibrate the top loading balance at 1g and 100g using Class 2 weights as outlined in the current revision of SOP-T043.

13.2.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.3. Pipetter

13.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment Calibration, Verification, and Monitoring."

13.4. pH Meter Initial Calibration

13.4.1. Calibrate the pH meter daily prior to sample analysis at pH of 4.00, 7.00, and 10.00 using fresh buffer solutions and according to the instrument manufacturer's recommended procedures.

13.4.2. Verify the calibration with fresh second source buffer standard. The second source standard shall not differ from its expected value by more than 0.05 pH units. If this criterion is not met, recheck calibration or effect corrective action.

13.4.3. The theoretical slope shall be within 90–105% for analysis to proceed. If this criterion is not met, determine the cause of the problem, effect corrective action, and recalibrate, if necessary.

13.5. Ion Chromatograph

13.5.1. Prior to the analysis of samples, a valid blank + multi-point calibration curve shall be established. The ICAL must be verified by a passing ICV and ICB standard, prior to sample analysis. Samples may not be analyzed until a valid calibration curve is established.

14. ▶PROCEDURE

14.1. Sample Preparation

14.1.1. Allow samples to reach ambient temperature prior to filtration and pH adjustment.

14.1.1.1. All samples and QC (MB, LCS, LCSD, Duplicates, MS, and MSD, as applicable) must be filtered and have the pH adjusted prior to analysis.

14.1.2. QC Samples (LCS, MS, and MSD) must be spiked prior to filtration and pH adjustment.

14.1.2.1. For the aqueous LCS and MS/MSD, add 100-µL buffer to 10 mL of the sample and spike with 50 µL of the second-source 10-ppm working standard; filter and transfer approximately 4 mL to an autosampler vial and analyze.

14.1.2.2. To filter QC and field samples: using a 10-mL disposable plastic syringe, draw approximately 8–10 mL of sample into the syringe by pulling back on the syringe plunger. Once the syringe is full, attach a 0.45-µm filter disk to the syringe tip. Slowly push down on the plunger until the sample begins to pass through the filter disk. Dispose of the first 0.5 mL of sample filtrate.

14.1.2.3. Continue pushing down on the plunger until the sample has passed through the filter disk and collect the filtrate in a 120-mL

plastic specimen container (if keeping additional filtrate for reanalysis) or directly into the autosampler vial. Do not use excessive force as the filter disk may rupture. Use a new syringe and filter disk for each sample.

14.1.2.4. Once filtered, adjust the pH of each field sample to between 9.0 and 9.5 by transferring 4 mL of filtrate into an autosampler vial and adding 40 µL of buffer solution (Section ***10.1.9.***) Use narrow-range pH paper to check the pH of the filtrate before and after adjustment by transferring a drop of filtrate onto the pH paper a capillary tube or disposable pipette. Record the initial and final pH values in the Sample Preparation Logbook.

14.1.2.4.1. If salts are formed as a result of pH adjustment, the samples must be filtered again to remove solids.

14.1.2.5. Once the filtrate has been sufficiently buffered, it is ready for analysis. Cap the vial and place on the autosampler.

14.2. Sample Analysis

14.2.1. ***Daily Retention Time Window***

14.2.1.1. ***The method retention time window must be updated prior to sample or standard processing.***

14.2.1.1.1. ***Following the analysis of the initial CCV, or using the midpoint calibration standard if a new ICAL was performed, update the retention time in the instrument method. See section 12.5. for additional information.***

14.2.2. ***ICAL or Opening CCV***

14.2.2.1. ***If the instrument requires calibration, proceed with the analysis of the calibration blank and then the sequential standards. Follow with the ICV/ICB. The ICAL must be valid prior to initiating sample and QC analyses.***

14.2.2.2. ***If the ICAL is not needed, the sequence will start with the analysis of a CCV, followed by a CCB. If these meet defined acceptance criteria, sample and QC analysis may proceed. A CCV/CCB pair must be analyzed every 10 samples (every 10 injections for certain programs) and at the end of the analytical sequence.***

14.2.3. Continuing Calibration (CCV) Analysis

14.2.3.1. The ICAL is continually verified through the analysis of continuing calibration verification standards (CCVs). The concentration of the CCV is at or near the midpoint of the curve (50ppb). Opening, bracketing, and closing CCV's are required to be analyzed.

14.2.3.2. The acceptance criterion for the CCV is a %D ≤ 10%.

14.2.3.2.1. If the CCV meets this criterion, sample analysis may continue. If the CCV fails, it should be reanalyzed, or reprepared and reanalyzed. If it fails again, the analytical system is considered out of control, perform corrective action and recalibrate. Samples may not be analyzed until a valid calibration curve is established.

14.2.3.2.2. If the bracketing/ending CCV does not meet acceptance criterion, then all sample data obtained since the last acceptable CCV must be invalidated and the samples reanalyzed.

14.2.3.2.2.1. If the closing CCV is high and the associated samples are ND, reanalyze the CCV to confirm. If still high or within criteria, report the ND data with narration. If low, reanalyze all samples with a passing CCV/ICAL. If there is insufficient sample volume remaining for reanalysis, then the data must be qualified and the QC issue addressed in the report narrative.

14.2.4. Continuing Calibration Blanks:

14.2.4.1. Satisfactory instrument baseline is continually assured through the analysis of continuing calibration blanks (CCBs). CCBs are reagent water with buffer solution added, without any preparatory steps. Opening, bracketing, and closing CCBs are required to be analyzed.

14.2.4.1.1. Prepare CCBs by diluting 1.0 mL of buffer to a final volume of 100mL with reagent water.

14.2.4.1.2. The acceptance criterion for CCBs is 0 ± MDL where MDL represents the current MDL value. If the CCB fails, it should be reanalyzed. If it fails again, the analytical system is considered out of control and the cause must be determined and corrected prior to the continued analysis of samples.

14.2.4.1.3. If the ending CCB still does not meet the acceptance criterion, then all sample data obtained since the last acceptable CCB must be invalidated and the samples reanalyzed with a passing CCB. However, as with the MB, if the CCB is positive, the CCV is within criteria, and the associated samples are ND, the data may be reported with narration.

This should be noted on the technical data review checklist and the PM should be notified.

14.3. Analysis Sequence

14.3.1. Autosampler vials are loaded onto the sample tray and analytic processing commenced. If an initial calibration has not been established, load the calibration standards and ICV/ICB prior to the analysis of client and QC samples.

14.3.2. In general, the following will apply to all sample sequences:

14.3.2.1. An instrument blank will be analyzed first, and it must be clean.

14.3.2.2. A calibration blank will be the first 'calibration standard' analyzed, and it will be included in the calibration curve.

14.3.2.3. The method blank will be analyzed immediately following the ICV/ICB or opening CCV/CCB.

14.3.2.4. An opening CCV/CCB pair will be analyzed along with bracketing, every 10 samples, and closing CCV/CCBs as per the sequence noted below, and corrective action performed if needed.

14.3.2.5. An LCS or LCS/LCSD pair will be analyzed for every batch of 20 samples.

14.3.2.6. An MS/MSD pair will be analyzed for every 10 field samples.

14.3.2.7. A batch will consist of a method blank, LCS or LCS/LCSD pair, two MS/MSD pairs and up to 20 field samples.

14.3.3. Run samples in the following or other logical order:

Instrument blank
*Cal Blank
*Cal Standard 1
*Cal Standard 2
*Cal Standard 3
*Cal Standard 4
*Cal Standard 5
*Cal Standard 6
*Cal Standard 7
*ICV
*ICB
CCV (Opening)
CCB
Method Blank
LCS
LCSD, when applicable
10 field samples
MS
MSD

CCV
CCB
10 field samples
CCV
CCB

* The initial calibration and ICV and ICB standards are only analyzed when the instrument needs to be calibrated. They are included in the daily analytical sequence table to assist with the data processing program.

14.4. Set up the ion chromatograph in preparation for the analytical sequence. Samples are injected one time. RPD data for duplicate injections is not captured/calculated.

14.5. Edit the sequence in the data system. After all correct sample, standard and consumable traceability information is entered, save the sequence.

14.6. After saving the sequence, print out a copy, stamp with the controlled stamp, three hole punch, and place in the run log binder.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window of the target analyte. The daily retention time window is the retention time of the analyte in the daily standard ± three times the mean standard deviation determined in the retention time window study.

14.8.1.1. Tentative identification of an analyte occurs when a peak from a sample or sample extract falls within the daily retention time window.

14.8.1.2. Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and effect appropriate corrective action.

14.8.2. Quantitation of the target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample or sample extract and the calibration standards.

14.8.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2. Determine the concentration based on the initial calibration curve.

14.8.2.3. If the instrument response for any client or QC sample exceeds the calibration range, dilute the sample and reanalyze.

15. ▶CALCULATIONS

15.1. The percent difference of the analyte is calculated as follows:

$$\%D = \frac{|C_m - C_t|}{C_t} X\,100$$

where: %D = percent difference (or percent drift) of the target analyte.
C_m = measured concentration of the target analyte (µg/L).
C_t = true concentration of the target analyte (µg/L).

15.2. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) x\,100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

15.3. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) x\,100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in the sample used.
C_{added} = concentration of target analyte added.

15.4. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} x\,100$$

where: RPD = relative percent difference between C_1 and C_2.
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.5. The concentration of the injected sample is read directly from the display and is calculated as follows:

$$C_f = C_d \times DF$$

where: C_f = final concentration in sample (µg/L).
C_d = concentration obtained directly from the display (µg/L).
DF = dilution factor.

15.6. All concentrations shall be reported in µg/L (ppb) for water samples.

15.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves as well as a full-length laboratory apron.

17.3.3. Face shield and or safety glasses.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to Section 12 for quality control requirements and corrective actions.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for soil and solid waste samples.

18.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS: Corrective action must be taken for an LCS failure. Because they denote whether the analytical system is operating within control, LCS recoveries must be within acceptance criteria, with the exceptions noted in section 12.3.1. If the recoveries fail, the group leader confirms the unacceptable result and initiates corrective action.

20.1.2. MS/MSD: Corrective action is not taken for MS/MSD failures if the LCS is within criteria. At that point, the MS/MSD failure is attributed to matrix effects—either reducing or oxidizing.

20.1.2.1. If the LCS and MS/MSD are all outside criteria then the samples require repreparation/reanalysis.

20.1.2.2. If there is insufficient sample volume for reanalysis, or repreparation and analysis, the QC issue should be addressed in the report narrative.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated

consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. US EPA, Method 218.6, Determination of Dissolved Hexavalent Chromium In Drinking Water, Ground Water and Industrial Wastewater Effluents by Ion Chromatography, Revision 3.3, May 1994.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. None.

24. MODIFICATIONS

24.1. None.

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
1.2	Minor typos corrected throughout. Section 3: Update detection limits. Section 5: Update method summary. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample container and storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Add data assessment. Section 20: Update contingencies. Section 24: Add Modifications. Section 25: Add Revision History.	K. Burney	2013-05-27
1.3	Section 6: Update definitions.	K. Burney	2014-01-20

Revision	Description (Cont.)	Author	Effective Date
1.3	Section 9: Update equipment. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 23: Add appendix. Section 25: Update Revision History.	K. Burney	2014-01-20
2.0	Entire SOP updated to include additional information and clarification as to procedures. See Bold Italicized type in each section and subsection.	L. Scharpenberg	2015-09-25

Title : **EPA METHOD 245.1, MERCURY (MANUAL COLD VAPOR TECHNIQUE)**

Document No. : SOP-M621
Revision No. : 0.0
Supersedes : None

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PROPRIETARY INFORMATION STATEMENT

APPROVED FOR RELEASE BY:

L. Lane
MANAGEMENT 09/14/07 **DATE**

QA DEPARTMENT 09-14-07 **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 245.1, Mercury (Manual Cold Vapor Technique).

2. APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface, ground, and saline waters, industrial and domestic wastes, and mobility-procedure extracts (TCLP/SPLP/WET extracts).

3. DETECTION LIMITS

3.1. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions.

3.2. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

4. SCOPE AND APPLICATION

4.1. EPA Method 245.1 is a cold vapor atomic absorption procedure that measures total mercury (organic and inorganic) in water.

4.1.1. Organo-mercury compounds do not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ion. Potassium permanganate oxidizes many of these compounds.

4.1.2. A number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by potassium permanganate. Potassium persulfate ensures the complete oxidation of these compounds.

4.2. For reference where this method is approved for use in compliance monitoring programs such as Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA), consult the appropriate sections of the Code of Federal Regulation Title 40 (40 CFR) and the latest Federal Register announcements.

4.2.1. For National Pollutant Discharge Elimination System (NPDES), consult 40 CFR Part 136 §136.3 Table 1B.

4.2.2. For drinking water, consult 40 CFR Part 141 §141.23.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of atomic absorption spectrometer, skilled in the interpretation of atomic absorption spectra, and knowledgeable in the correction of interferences described in this method.

5. METHOD SUMMARY

5.1. Cold-vapor atomic absorption (CVAA) technique is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.2. A known portion of a water sample is transferred to a digestion vessel. It is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for two hours at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury, and is measured by the cold vapor atomic absorption technique.

5.3. Prior to analysis, samples must be digested using the appropriate sample preparation method. The preparatory method is described in Section 14.1.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.12. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.13. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.14. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.15. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.16. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.17. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.18. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a

product or service meets defined standards of quality with a stated level of confidence.

6.19. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.20. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.21. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.22. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.23. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.24. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.25. Terms Specific to Mercury Analysis

6.25.1. Linear Dynamic Range: The concentration range over which the analytical curve remains linear.

6.25.2. Method of Standard Addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard.

6.25.3. Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

6.25.4. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.25.5. Sensitivity: The concentration of metal, in mg/L, that produces absorption of 1%.

7. INTERFERENCES

7.1. Interferences have been reported for waters containing sulfide, chloride, copper, and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. Since the concentration levels for interferants are difficult to define, the quality control procedures must be strictly followed.

7.1.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

7.1.2. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

7.1.2.1. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).

7.1.3. Copper concentrations as high as 10 mg/L has no effect on the recovery of mercury from spiked samples.

7.2. Certain volatile organic materials that absorb at 253.7 nm may also cause interference.

7.2.1. A preliminary run without reagents can determine whether this type of interference is present.

7.2.2. The dead air space in the digestion vessel should be purged prior to the addition of stannous chloride solution to remove any interfering volatile materials.

7.3. Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD).

8. SAFETY

8.1. Mercury compounds are highly toxic. Hence, precautions must be taken to avoid mercury ingestion, inhalation, or absorption through the skin.

8.2. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples containing mercury must be performed in a fume hood vented to the exterior of the laboratory.

8.3. All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Atomic Absorption Spectrometer: Perkin-Elmer Flow Injection Mercury System (FIMS) 400 or equivalent configured with the following components:

9.1.1. Mercury lamp, high intensity.

9.1.2. Absorption cell, long path, quartz.

9.1.3. Peristaltic pump.

9.1.4. Autosampler, Perkin-Elmer AS-90 or equivalent.

9.1.5. Autosampler vessels, 17-mm diameter (15-mL capacity) and 25-mm diameter (50-mL capacity), polypropylene.

9.1.6. Argon gas supply, high purity.

9.1.7. PC based data system or equivalent.

9.2. Graduated cylinders, various sizes, Class A.

9.3. Volumetric flask, 100-mL, glass, Class A.

9.4. Thermometer.

9.5. Block digester, equipped with water bath, capable of maintaining 95°C.

9.6. Vial, 120-mL, polypropylene, with polypropylene closures, disposable.

9.6.1. The vial is used for sample preparation (digestion).

9.7. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.8. Pipetters, 100–1000-µL and 0.5–5.0-mL, adjustable, with disposable tip.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Sulfuric acid, H_2SO_4, concentrated, trace metal grade or equivalent.

10.1.2. Hydrochloric acid, HCl, concentrated, trace metal grade or equivalent.

10.1.3. Hydrochloric acid, HCl, 3% (v/v).

10.1.3.1. Prepare the solution by slowly adding 30 mL of concentrated HCl to 500 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.3.2. This solution is used as the carrier solution for the instrument.

10.1.3.3. It is also used as a rinse blank to flush the system between standards and samples to minimize interferences.

10.1.4. Nitric acid, HNO_3, concentrated, trace metal grade or equivalent.

10.1.5. Stannous chloride, $SnCl_2$.

10.1.5.1. Prepare the mixture by adding 11 g of stannous chloride (reagent grade or equivalent) to 1000 mL of 3% HCl.

10.1.5.2. Stannous sulfate may be used in place of stannous chloride.

10.1.5.3. This mixture is used as the reducing agent for the instrument.

10.1.6. Sodium chloride-hydroxylamine hydrochloride, $NaCl\text{-}H_3NO\cdot HCl$.

10.1.6.1. Prepare the solution by dissolving 12 g of sodium chloride (reagent grade or equivalent) and 12 g of hydroxylamine hydrochloride (reagent grade or equivalent) in reagent water and dilute to 100 mL with additional reagent water.

10.1.6.2. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

10.1.7. Potassium permanganate, $KMnO_4$, 5% (w/v), mercury free.

10.1.7.1. Prepare the solution by dissolving 5 g of potassium permanganate (reagent grade or equivalent) in 100 mL of reagent water.

10.1.8. Potassium persulfate, $K_2S_2O_8$, 5% (w/v).

10.1.8.1. Prepare the solution by dissolving 5 g of potassium persulfate (reagent grade or equivalent) in 100 mL of reagent water.

10.1.9. Reagent water, interferant free, nano-pure.

10.1.10. Chips, Teflon.

10.1.11. Beads, glass.

10.1.12. All reagents must be inspected and documented prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions (ultra-high purity grade or equivalent), each in sealed polyethylene bottles, containing 100 ppm of mercury are used to prepare calibration and check standards.

10.2.1.1. Prepare the 2-ppm mercury working standard solution by diluting 2 mL of the 100-ppm mercury stock standard solution and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.1.2. Prepare the second source 1-ppm mercury working standard solution by diluting 1 mL of the second source 100-ppm mercury stock standard solution and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Transfer 0.5 mL of the 2-ppm mercury working standard solution to a clean 120-mL vial containing reagent water, and dilute to 50 mL with additional reagent water. Mix thoroughly.

10.2.2.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the vial and mix.

10.2.2.3. Slowly add 1.25 mL of concentrated HNO_3 to the vial and mix.

10.2.2.4. Add 7.5 mL of 5% $KMnO_4$ solution to the vial, and allow it to stand for at least 15 minutes.

10.2.2.5. Add 4 mL of 5% $K_2S_2O_8$ solution to the vial.

10.2.2.6. Place the vial in the block digester and heat for 2 hours in the water bath maintained at 95°C.

10.2.2.7. When the solution is cooled, add 3 mL of sodium chloride-hydroxylamine hydrochloride to the vial to reduce excess permanganate.

10.2.2.8. Obtain the 10-ppb mercury calibration standard solution by adjusting the volume to 100 mL with calibration blank.

10.2.2.9. Prepare the initial calibration standard solutions by diluting appropriate volumes of the 10-ppb mercury calibration standard solution with calibration blank.

Initial Calibration Standard				
Element	Initial Conc. (ppb)	Initial Volume (mL)	Final Conc. (ppb)	Final Volume (mL)
Mercury Hg	10.0	1.0	0.5	20.0
	10.0	2.0	1.0	20.0
	10.0	4.0	2.0	20.0
	10.0	10.0	5.0	20.0
	10.0	20.0	10.0	20.0

10.2.2.10. The 2.0-ppb standard is also used as the continuing calibration verification solution.

10.2.3. Calibration Blank (CB)

10.2.3.1. Transfer 50 mL of reagent water to each of the several clean 120-mL vials.

10.2.3.2. Slowly add 2.5 mL of concentrated H_2SO_4 to each vial and mix.

10.2.3.3. Slowly add 1.25 mL of concentrated HNO_3 to each vial and mix.

10.2.3.4. Add 7.5 mL of 5% $KMnO_4$ solution to each vial, and allow it to stand for at least 15 minutes.

10.2.3.5. Add 4 mL of 5% $K_2S_2O_8$ solution to each vial.

10.2.3.6. Place the vials in the block digester and heat for 2 hours in the water bath maintained at 95°C.

10.2.3.7. When the solution is cooled, add 3 mL of sodium chloride-hydroxylamine hydrochloride to each vial to reduce excess permanganate.

10.2.3.8. The CB is used to establish the zero point of the calibration curve or to dilute standards and samples.

10.2.3.9. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.4. Method Blank (MB)

10.2.4.1. Prepare the MBs as described in Section 14.1.

10.2.4.2. The MB is used to identify possible contamination resulting from either the reagents or the equipment used during sample processing.

10.2.5. Initial Calibration Verification (ICV) Solution

10.2.5.1. Transfer 0.5 mL of the second source 1-ppm mercury working standard solution to a clean 120-mL vial containing reagent water, and dilute to 50 mL with additional reagent water. Mix thoroughly.

10.2.5.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the vial and mix.

10.2.5.3. Slowly add 1.25 mL of concentrated HNO_3 to the vial and mix.

10.2.5.4. Add 7.5 mL of 5% $KMnO_4$ solution to the vial, and allow it to stand for at least 15 minutes.

10.2.5.5. Add 4 mL of 5% $K_2S_2O_8$ solution to the vial.

10.2.5.6. Place the vial in the block digester and heat for 2 hours in the water bath maintained at 95°C.

10.2.5.7. When the solution is cooled, add 3 mL of sodium chloride-hydroxylamine hydrochloride to the vial to reduce excess permanganate.

10.2.5.8. Obtain the 5.0-ppb ICV solution by adjusting the volume to 100 mL with calibration blank.

10.2.6. Continuing Calibration Verification (CCV) Solution

10.2.6.1. Prepare the 2.0-ppb CCV solution by diluting 4.0 mL of the 10-ppb mercury calibration standard solution (see Section 10.2.2.) to 20.0 mL with calibration blank.

10.2.7. Linear Dynamic Range Solutions

10.2.7.1. Prepare a minimum of three different concentrations of the linear dynamic range solutions in the same acid matrix by diluting the 1-ppm mercury working standard solution. The analyst determines the applicable concentrations.

10.2.7.2. The linear dynamic range solutions contain various concentrations of mercury. They are used to establish linear dynamic range (see Section 12.4.).

10.2.8. Spike Standard Solution

10.2.8.1. Use the 2-ppm mercury working standard solution as the spike standard solution.

10.2.8.2. The spike standard solution are used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

10.2.8.3. Add 250 µL of the spike standard to each 10-mL aliquot of MS/MSD leachate (TCLP/SPLP/WET extract) prior to dilution and acidification.

10.2.8.4. Add 250 µL of the spike standard to each 10-mL aliquot of aqueous MS/MSD and LCS/LCSD sample prior to digestion.

10.2.8.5. Add 25 µL of the spike standard to each 10-mL aliquot of PDS digestate.

10.2.9. The 2-ppm and 1-ppm working standards must be replaced after six months or sooner if comparison with check standards indicates a problem. All other standards must be prepared fresh daily.

10.2.10. All stock standards must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene containers with Teflon-lined closures. Soil and other non-aqueous samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.

11.1.1. Aqueous samples shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2. Samples should be maintained in a chilled state ($\leq$4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a 4°C cooler. Samples must be digested and analyzed within 28 days of collection.

12. QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established daily prior to the processing of samples.

12.1.1.1. The calibration curve is established with one calibration blank and five calibration standards.

12.1.2. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression is ≥0.995.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤5%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibration, if necessary.

12.3. Initial Calibration Blank (ICB)

12.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > ½ RL (or the limit specified in the project specific DQO).

12.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Reprepare and reanalyze the ICB.

12.4. Linear Dynamic Range

12.4.1. Following the initial instrument setup, the upper limit of the linear dynamic range for mercury must be established prior to initial calibration.

12.4.1.1. The upper range limit is established by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range.

12.4.1.2. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file.

12.4.2. Following the establishment of a valid initial calibration, the upper range limit must be checked annually, and a new upper range limit should be determined whenever there is a significant change in instrument response.

12.4.3. The upper range limit is deemed valid if the %D for each analyte in a high-level check standard analyzed and quantitated against the calibration curve is ≤10%.

12.5. Continuing Calibration Verification (CCV)

12.5.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence.

12.5.2. The initial calibration is deemed valid if the %D for each analyte is ≤10%.

12.5.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Effect corrective action and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, recalibrate.

12.6. Continuing Calibration Blank (CCB)

12.6.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > ½ RL (or the limit specified in the project specific DQO).

12.6.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Reprepare and reanalyze the CCB.

12.7. Event Based Quality Control (LCS/LCSDs and MBs)

12.7.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.7.2. The acceptance criteria for LCS/LCSD elements are as follows:

12.7.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.7.2.1.1. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤20%.

12.7.2.2. All LCS/LCSD elements must be within acceptance limits.

12.7.3. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of the target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.7.3.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.7.3.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.8. Matrix Based Quality Control (MS/MSDs and PDSs)

12.8.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.8.2. The acceptance criteria for MS/MSD elements are as follows:

12.8.2.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.8.2.1.1. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤20%.

12.8.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.8.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.8.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.9. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.10. Dilution Test

12.10.1. If the analyte concentration is sufficiently high, an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.10.2. If this criterion is not met, an interference effect shall be suspect. Perform recovery test.

12.11. Recovery Test (Post Digestion Spike Addition)

12.11.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution.

12.11.2. The acceptance criteria for PDS elements are as follows:

12.11.2.1. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

12.11.2.2. If the %REC of the PDS element is not within the established acceptance limits, a matrix effect shall be suspect. Perform MSA on all samples within the batch.

12.12. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T042, "Thermometer Calibration."

13.3. Pipetter

13.3.1. Calibrate the pipetter according to the procedure outline in the pipetter calibration logbook.

13.4. Spectrometer Initial Calibration

13.4.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.4.2. After obtaining an acceptable five-point calibration curve and prior to processing sample or QC digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.

13.4.3. The initial five-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Sample Preparation (Digestion)

14.1.1. Transfer 50 mL of well-mixed aqueous sample to a clean 120-mL vial.

14.1.1.1. For MB/LCS/LCSD, transfer 50 mL of clean reagent water.

14.1.1.1.1. If TCLP/SPLP/WET extraction was performed on the MB sample (aqueous or solid), transfer 10 mL of the resulting MB extract.

14.1.1.2. For MS/MSD/PDS, transfer 50 mL of aqueous sample in each analytical batch selected for spiking.

14.1.1.2.1. If TCLP/SPLP/WET extraction was performed on the MS/MSD/PDS sample (aqueous or solid), transfer 10 mL of the resulting MS/MSD/PDS extract.

14.1.2. Record the volume to the nearest 1 mL.

14.1.3. Add the appropriate amount of the spike standard solution (Section 10.2.7.) to the MS/MSD sample.

14.1.3.1. If TCLP/SPLP/WET extraction was performed on the MS/MSD sample (aqueous or solid), the resulting MS/MSD extract should be spiked prior to acid preservation.

14.1.4. Slowly add 2.5 mL of concentrated H_2SO_4 to the vial and mix.

14.1.5. Slowly add 1.25 mL of concentrated HNO_3 to the vial and mix.

14.1.6. Add 7.5 mL of 5% $KMnO_4$ solution to the vial, and allow it to stand for at least 15 minutes.

14.1.6.1. Sewage samples may require additional permanganate.

14.1.6.2. Ensure that equal amounts of permanganate are added to calibration standards, calibration verification standards, calibration blanks, QC check samples, and method blanks.

14.1.7. Shake and add additional portions of 5% $KMnO_4$ solution to the vial, if necessary, until the purple color persists for at least 15 minutes.

14.1.8. Add 4 mL of 5% $K_2S_2O_8$ solution to the vial.

14.1.9. Place the vial in the block digester and heat for 2 hours in the water bath maintained at 95°C.

14.1.10. When the digestate is cooled, add 3 mL of sodium chloride-hydroxylamine hydrochloride to the vial to reduce excess permanganate.

14.1.11. Add the appropriate amount of the spike standard solution (Section 10.2.7.) to the PDS digestate.

14.1.12. Dilute the digestate to 100 mL with calibration blank.

14.1.13. Transfer sufficient amount of the diluted digestate to a clean autosampler vessel for analysis.

14.2. Instrument Setup

14.2.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 15 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.2.1.1. Argon gas supply is set at 45 psi.

14.2.1.2. Wavelength for mercury absorbance measurement is set at 253.7 nm.

14.2.1.3. Autosampler is set to inject 500 µL of sample or QC digestate.

14.2.2. Place the inlet of the blue/yellow carrier pump tube in the 3% HCl reservoir. Place the inlet of red/red reductant pump tube in the stannous chloride reservoir. Position the sampling probe in the reagent water reservoir.

14.2.2.1. Adjust the carrier flow rate to 9−11 mL/min, and the reductant flow rate to approximately one half of the carrier flow rate (5−7 mL/min).

14.2.2.2. The flow rate can be checked by placing the inlet of the tube in a graduated cylinder filled with reagent water, and then measuring the volume decrease after one minute.

14.2.2.3. If the flow rate is not within the appropriate range, adjust the pump pressure for the tube until the flow rate is within range.

14.2.3. Program the system to average at least duplicate readings on samples including the calibration standards, the calibration verification standards, the calibration blanks, the QC check samples and method blanks. Report the average.

14.2.3.1. If the %RSD for an analyte in a standard is > 10%, re-analyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.2.3.2. If the %RSD for an analyte in a sample is > 20%, re-analyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.3. Establish a calibration curve to cover the appropriate concentration range (see Section 13.4.).

14.4. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.5. and Section 12.6.

14.4.1. If a CCV/CCB fails, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.5. Following digestion by the procedure specified in Section 14.1., the digestates for the QC and actual environmental samples are received in autosampler vessels. The autosampler vessels are then loaded onto the system sample tray.

14.6. Sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Method Blank (MB)
6) Laboratory Control Samples (LCS)
7) Laboratory Control Sample Duplicates (LCSD)
8) Matrix Spike (MS)
9) Matrix Spike Duplicate (MSD)
10) Post Digestion Spike (PDS)
11) Samples (up to 10, including QC check samples and MBs)
12) Continuing Calibration Verification (CCV)
13) Continuing Calibration Blank (CCB)
14) Samples (up to 10, including QC check samples and MBs)
15) Ending CCV
16) Ending CCB

14.6.1. Item 1: The CB is a vial of reagent water digestate used to establish the zero point of the initial calibration curve.

14.6.2. Item 2: The initial calibration standards are used to establish the initial calibration curve.

14.6.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial five-point calibration. An acceptable ICV is required daily after initial calibration.

14.6.4. Item 4: The ICB is a vial of reagent water digestate used to monitor contamination. An acceptable ICB is required daily after initial calibration verification.

14.6.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.6.5.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of clean Teflon chips (or glass beads).

14.6.5.2. One MB is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.6.5.3. When samples that are leached/digested together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water digestate must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.6.6. Item 6: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.6.6.1. For aqueous samples, the LCS consists of the specified element spiked into clean reagent water. For solid samples, the LCS consists of the specified element spiked into clean Teflon chips (or glass beads).

14.6.6.2. One LCS is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.6.7. Item 7: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.6.8. Item 8: The MS is an actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.6.8.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.6.8.2. One MS is required for every batch of 20 samples per matrix or portion thereof digested/leached concurrently.

14.6.9. Item 9: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.6.10. Item 10: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentration of specific target analyte post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.6.10.1. The purpose of the PDS is to access matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.6.10.2. One PDS is required for the occurrence of new or unusual matrix included within the batch, or for the failure of dilution test or matrix spike recovery.

14.6.11. Items 11 and 14: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.6.12. Items 12 and 15: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.6.13. Items 13 and 16: A CCB is a vial of reagent water digestate used to monitor contamination. An acceptable CCB is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.6.14. Rinse blanks consisting of 3% HCl solution may be added elsewhere in the sequence to rinse the analytical system.

14.7. Ensure that sufficient amounts of 3% HCl solution and stannous chloride mixture are present in the 3% HCl and stannous chloride reservoirs, respectively, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.8. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.9. Initiate the sequence.

14.10. Dilution and recovery tests (see Section 12.10. and Section 12.11.) are recommended prior to reporting concentration data for the elements.

14.10.1. It is recommended that these tests should be performed with each batch of samples prepared/analyzed to ensure that neither positive nor negative interferences are affecting the measurement of any element or distorting the accuracy of the reported values.

14.11. Method of Standard Additions (MSA)

14.11.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a digested sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.11.1.1. The MSA may be appropriate for analyses of extracts, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the dilution or recovery test.

14.11.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.8. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.11.3. Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix A. A linear regression program may be used to obtain the intercept concentration.

14.11.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.11.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.11.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.11.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

14.12. Data Interpretation

14.12.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between absorbances in the sample digestate and the calibration standards.

14.12.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the absorbance of an element can be determined.

14.12.1.2. Determine the concentration based on the initial calibration curve.

14.12.1.2.1. The data system is programmed to perform the calculation of concentration.

14.12.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{A_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the absorbance readings for the target analyte.
A_{ave} = mean of the absorbance readings for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.7. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in g.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of solution A.
S_B = analytical signal (corrected for the blank) of solution B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.9. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.9.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and mg/kg (ppm) on a dry-weight basis for soil samples.

15.10. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S. All LCS/LCSD elements must be within acceptance limits.

18.1.1. For EPA Region 9 requirement, refer to Section 12.7.2.1.1. for acceptance criteria.

18.1.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated

samples are not detected, the sample data can be reported without qualification.

18.1.3. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of the target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.3. The acceptance criteria for MS/MSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S. All MS/MSD elements must be within acceptance limits.

18.3.1. For EPA Region 9 requirement, refer to Section 12.8.2.1.1. for acceptance criteria.

18.3.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

18.4.1. When the %REC of the PDS elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The PDS data shall be reported with the corresponding sample data.

18.4.2. If the %REC of the PDS elements are not within the established acceptance limits, the MSA results shall be reported with the corresponding sample data.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly

evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and mg/kg (ppm) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample

disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Mercury (Manual Cold Vapor Technique)*, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Method 245.1, USEPA, March 1983.

22.2. *Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry*, Methods for the Determination of Metals in Environmental Samples, Supplement I, EPA 600/R-94-111, Method 245.1, USEPA, Revision 3, May 1994.

22.3. *Mercury in Water by Manual Cold Vapor Atomic Absorption (CVAA)*, Method 245.1, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, March 2001.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Standard Addition Plot (Example).

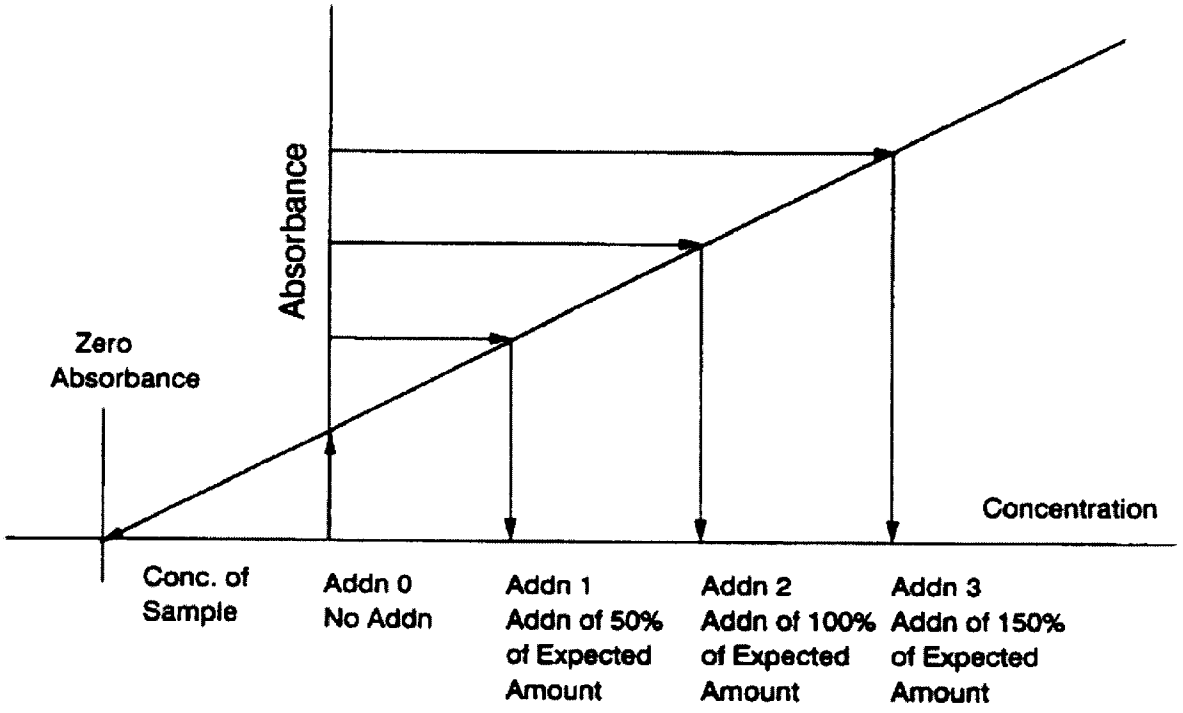
Appendix A

STANDARD ADDITION PLOT (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix A

Standard Addition Plot (Example)



Title : **EPA METHOD 300.0/9056, DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY**

Document No. : SOP-M703
Revision No. : 5.1
Supersedes : 5.0

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PROPRIETARY INFORMATION STATEMENT

Revision 5.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 5/2/2016
MANAGEMENT **DATE**

_____ 04-29-16
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 300.0/9056, Determination of Inorganic Anions by Ion Chromatography.

2. APPLICABLE MATRICES

2.1. EPA Method 300.0 is applicable to drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction), and leachates (when no acetic acid is used).

2.2. EPA Method 9056 is applicable to drinking water, wastewater, and aqueous extracts of solids.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for these methods are as follows:

	Aqueous	Aqueous (Refinery)	Solid
Chloride	1.0 mg/L	10 mg/L	10 mg/kg (wet-weight)
Sulfate	1.0 mg/L	10 mg/L	10 mg/kg (wet-weight)
Other Anions	0.10 mg/L	1.0 mg/L	1.0 mg/kg (wet-weight)

3.2. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 300.0 and EPA Method 9056 are used to determine the concentrations of common inorganic anions in a variety of matrices.

4.2. The following analytes are routinely determined by these methods.

Bromide (Br^-)
Chloride (Cl^-)
Fluoride (F^-)
Nitrate (NO_3^-) as N
Nitrite (NO_2^-) as N
ortho-Phosphate (PO_4^{3-}) as P
Sulfate (SO_4^{2-})

4.3. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added analytes lend themselves to EPA Method 300.0 or EPA Method 9056 determination, either by regulatory reference or validation studies.

4.4. These methods are restricted to use by or under the supervision of analysts experienced in the use of ion chromatograph (IC) and skilled in the interpretation of ion chromatograms.

5. METHOD SUMMARY

5.1. EPA Method 300.0 and EPA Method 9056 describe chromatographic procedures that will allow for the separation of common anions and for their quantitative analysis by ion chromatography. Detection is achieved using a conductivity detector.

5.1.1. The preparation and analytical approaches are similar between both methods. Differences are found in certain quality control criteria as specified in Section 12.

5.2. Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.

5.2.1. Aqueous samples are filtered through a 0.22-µm filter and analyzed via direct injection.

5.2.1.1. Refinery aqueous samples are pretreated with hydrogen peroxide to remove sulfide prior to filtration.

5.2.1.2. Aqueous samples that appear to be turbid should be filtered through a 0.45-µm filter first prior to filtering through a 0.22-µm filter.

5.2.2. Solid samples are extracted using reagent water and filtered through a 0.22-µm filter. The filtered extracts are analyzed via direct injection.

5.2.2.1. Solid sample extracts that appear to be turbid should be filtered through a 0.45-µm filter first prior to filtering through a 0.22-µm filter.

6. DEFINITIONS

6.1. Refer to the current version of the Eurofins Calscience Quality Systems Manual for definitions and glossaries.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.2. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. A large amount of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

7.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated chromatographic baseline.

7.4. Water from the sample injection will cause a negative peak (dip) in the baseline when it elutes because its conductance is less than that of the suppressed eluent. Any ion of interest, especially fluoride, eluting near the negative water peak must be

sufficiently resolved from the negative water peak to be accurately quantified. Alternatively, the negative water peak can be eliminated by adding an equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample.

7.5. Samples that contain particles larger than 0.45-µm, and reagent solutions that contain particles larger than 0.20-µm require filtration to prevent damage to instrument columns and flow systems.

7.6. Any anion that is not retained or only slightly retained by the column will elute in the range for fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentration of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the analyst to generate precision and accuracy information in each sample matrix.

7.7. The acetate, formate, and other monovalent organic acid anions elute early during the chromatographic run. The retention times of the anions may differ when large amounts of acetate are present. Therefore, these methods are not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

7.8. Bromide and nitrate elute close to one another and thus can be potential interferences for each other. It is advisable to avoid having a bromide to nitrate ratio greater than 1:10 or 10:1 if both anions are to be quantified. If nitrate interferences are noted with bromide, the use of an electrochemical detector is recommended.

7.9. Samples containing high levels of potassium permanganate may interfere with the accurate quantitation of the anionic species and may lead to biased high results. This interference appears to be due to a reaction of permanganate with the post-column reagent that gives a colored species with much less absorbance.

7.9.1. Samples containing high levels of permanganate may be effectively treated with ascorbic acid. However, the amount of ascorbic acid should not exceed more than 1000mg/L due to potential negative effects on the instrumentation.

7.10. The quantitation of unretained peaks should be avoided. These include low molecular weight organic acid anions such as formate, acetate, propionate, etc. These anions are conductive and will coelute with or near fluoride and will bias the fluoride quantitation in some drinking water and most wastewaters.

7.11. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample should be purged with an inert gas (argon or nitrogen) for approximately 5 minutes or until no chlorine dioxide remains.

7.12. Decreases in retention times and resolution are symptoms of column deterioration which may be caused by the buildup of contaminants on the exchange resin. Refer to the manufacturer's guidelines for instructions on cleaning the column resin and column filter beds or replace the column when signs of declining performance are evident.

7.13. Refer to Appendix A for other potential interferences.

8. SAFETY

8.1. The eluent used in the ion chromatograph is basic (pH 10) and can cause eye and skin irritation.

8.2. No compounds covered by this method have been tentatively classified as known or suspected human carcinogens.

8.3. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g., safety glasses or goggles) and protective apparel (e.g., laboratory coats) are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling samples and chemicals.

8.4. Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the SDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Ion Chromatograph: Dionex ICS-1000 High Performance Integrated Ion Chromatography System configured with the following components:

9.1.1. Serial dual-piston pump, variable speed, 100 µL per revolution.

9.1.2. Anion self-regenerating suppressor, 4-mm, 0.5–3.0-mL/min flow rate, ≤ 200-µeq maximum suppression capacity, Dionex ASRS® 300 Anion Self-Regenerating Suppressor or equivalent.

9.1.2.1. For Dionex AS14A anion analytical column, the recommended "8.0-mM Na_2CO_3 / 1.0-mM $NaHCO_3$" eluent flow rate is 1.0 mL/min.

9.1.3. Sample injection loop, 25-µL.

9.1.4. Injection valve.

9.1.5. Autosampler, Dionex AS40 Automated Sampler or equivalent.

9.1.6. Autosampler cassettes, capable of holding 5.0-mL autosampler vials.

9.1.7. Autosampler vials, 5.0-mL capacity, with polyethylene caps and 20-µm sintered polyethylene filters, polypropylene, disposable.

9.1.7.1. Autosampler vials must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.

9.2. Instrument Software

9.2.1. Require a PC based data system or equivalent.

9.2.2. Dionex Chromeleon Chromatography Management System Version 6.50, Dionex Chromeleon Chromatography Management System Version 6.80, ***Thermo Scientific Dionex Chromeleon 7 Chromatography Data System Version 7.2.0.3765***, or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. Primary Detection Channel

9.4.1. Detector: Electric conductivity cell detector (ECD), Dionex DS6 Heated Conductivity Cell or equivalent.

9.4.2. Anion Analytical Column: 4-mm × 250-mm, 7.0-µm particle diameter, 120-µeq/column capacity, alkyl quaternary ammonium functional group, moderate hydrophobic, Dionex IONPAC® AS14A Analytical Column or equivalent.

9.4.3. Guard Column: 4-mm × 50-mm, 7.0-µm particle diameter, 24-µeq/column capacity, alkyl quaternary ammonium functional group, moderate hydrophobic, Dionex IONPAC® AG14A Guard Column or equivalent.

9.5. Reservoir Pressurized Gas: Helium, He, 99.995%, compressed, Praxair 4.5 grade or equivalent.

9.6. Graduated cylinders, 50-mL 100-mL, 500-mL, or other capacity, glass, Class A.

9.7. Volumetric flasks, 10-mL, 100-mL, 250-mL, 2-L, or other capacity, Class A.

9.8. Specimen containers, 4.5-oz (120-mL), high density polyethylene (HDPE) or polypropylene, with polypropylene lids, disposable.

9.9. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.10. Pipetters, 25-µL and 50-µL, fixed volume, with disposable tips.

9.11. Pipetters, 10−100-µL, 100−1000-µL, and 0.5−5.0-mL, adjustable volume, with disposable tips.

9.12. Pipets, transfer, plastic, disposable.

9.13. Tissue wipers, 1-ply, antistatic, VWR® Light-Duty Wipes Tissue Wipers or equivalent.

9.14. Wash bottle, 250-mL or other capacity.

9.15. Drying oven, capable of maintaining 104 ± 1°C.

9.16. Watch glass.

9.17. Desiccator.

9.18. Forceps or tongs, stainless steel.

9.19. Gloves, heat resistant.

9.20. Refer to Appendix A for additional equipment and supplies.

9.21. All critical supplies and consumable materials that have the potential of introducing contaminants must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure, with resistivity ≥ 17.8 MΩ-cm.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium carbonate, Na_2CO_3, anhydrous, fine white granules, certified reagent grade or equivalent.

10.1.4. Sodium bicarbonate, $NaHCO_3$, fine white crystals, certified reagent grade or equivalent.

10.1.5. Anion eluent concentrate, $Na_2CO_3/NaHCO_3$, 0.80-M/0.10-M, clear colorless liquid, commercially or manually prepared, Dionex AS14A Eluent Concentrate (100X) P/N 056937 or equivalent.

10.1.5.1. Prepare the anion eluent concentrate by dissolving the appropriate masses of Na_2CO_3 and $NaHCO_3$ in reagent water and diluting to the final volume with additional reagent water.

10.1.5.2. Use the following table as guidance to prepare the anion eluent concentrate.

Anion Eluent Concentrate	Molar Mass (g/mol)	Initial Mass (g)	Molar Conc (mol/L)	Final Vol (L)
Eluent Concentrate			0.80/0.10	2
Na_2CO_3	105.99	169.5840	0.80	
$NaHCO_3$	84.01	16.8020	0.10	

10.1.6. Eluent working solution, $Na_2CO_3/NaHCO_3$, 0.008-M/0.001-M.

10.1.6.1. Prepare the eluent working solution by diluting the appropriate volume of the anion eluent concentrate to the final volume with reagent water.

10.1.6.2. Use the following table as guidance to prepare the eluent working solution.

Eluent Working Solution	Initial		Final	
	Conc (mol/L)	Vol (mL)	Conc (mol/L)	Vol (L)
Working Solution			0.008/0.001	1
Eluent Concentrate	0.80/0.10	10		

10.1.7. Sodium fluoride, NaF, fine white powder, certified reagent grade or equivalent.

10.1.8. Sodium chloride, NaCl, fine white crystals, certified reagent grade or equivalent.

10.1.9. Sodium bromide, NaBr, fine white granules, certified reagent grade or equivalent.

10.1.10. Sodium nitrate, $NaNO_3$, fine white crystalline powder, certified reagent grade or equivalent.

10.1.11. Sodium nitrite, $NaNO_2$, fine yellow-white crystals, certified reagent grade or equivalent.

10.1.12. Potassium sulfate, K_2SO_4, white crystals, certified reagent grade or equivalent.

10.1.13. Potassium phosphate monobasic, KH_2PO_4, white crystals, certified reagent grade or equivalent.

10.2. Standards

10.2.1. Stock Standards

10.2.1.1. Use the certified salts (neat solids) or equivalent to prepare the stock standards.

10.2.1.2. Dry sufficient mass of each salt at 103–105°C for at least 1 hour and cool in a desiccator prior to the stock standard preparation.

10.2.1.3. Prepare each primary and second source stock standard solution by dissolving the appropriate masses of the salts in reagent water in a 250-mL volumetric flask and dilute to volume with additional reagent water.

10.2.1.3.1. Place a clean 250-mL volumetric flask on an analytical balance and tare.

10.2.1.3.2. Measure the appropriate mass of each salt into the volumetric flask. Tare the balance between each weighing.

10.2.1.3.3. Add 100–200 mL of reagent water. While holding the neck of the volumetric flask, swirl the contents until the solids have dissolved completely.

10.2.1.3.4. Dilute to 250 mL with additional reagent water.

10.2.1.3.5. Cap the volumetric flask and invert a minimum of three times to mix thoroughly.

10.2.1.3.6. Alternatively, prepare each stock standard solution gravimetrically by weighing the appropriate masses of the salts into a specimen container and add 250 mL of reagent water using a calibrated pipetter.

10.2.1.4. Use the following table as guidance to prepare the stock standards.

Compound / Anion	Molar Mass (g/mol)	
	Compound	Anion
NaF / F^-	41.99	19.00
NaCl / Cl^-	58.44	35.45
NaBr / Br^-	102.89	79.90
$NaNO_3$ / NO_3^- as N	84.99	14.01
K_2SO_4 / SO_4^{2-}	174.26	96.06
$NaNO_2$ / NO_2^- as N	69.00	14.01
KH_2PO_4 / PO_4^{3-} as P	136.09	30.97

Stock Standard	Initial Mass (g)	Final Conc (mg/L)	Final Vol (mL)
Stock #1		1000–20000	250
F^-	0.5525	1000	
Cl^-	8.2426	20000	
Br^-	0.6439	2000	
NO_3^- as N	3.0332	2000	
SO_4^{2-}	9.0704	20000	
Stock #2		1000	250
NO_2^- as N	1.2313	1000	
PO_4^{3-} as P	1.0986	1000	

10.2.1.5. Store the stock standard #1 in a sealed amber glass bottle under dark and refrigerated conditions, and replaced after six months or sooner.

10.2.1.6. Store the stock standard #2 in a sealed amber glass bottle under dark and refrigerated conditions, and replaced after one month or sooner.

10.2.2. Working Standards

10.2.2.1. Prepare each primary and second source working standard solution by measuring the appropriate volumes of the stock standards into a 100-mL volumetric flask and dilute to volume with reagent water.

10.2.2.1.1. Measure the appropriate volume of each stock standard (i.e., stock standards #1 and #2) into a clean 100-mL volumetric flask using a calibrated pipetter.

10.2.2.1.2. Dilute to 100 mL with reagent water.

10.2.2.1.3. Cap the volumetric flask and invert a minimum of three times to mix thoroughly.

10.2.2.1.4. Alternatively, prepare each working standard solution by measure the appropriate volume of each stock standard into a clean specimen container using a calibrated pipetter, place the specimen container on an analytical balance and tare, and carefully add 100 g of reagent water.

10.2.2.2. Use the following tables as guidance to prepare the working standards.

	Initial		Final	
Working Standard	Conc (mg/L)	Vol (µL)	Conc (mg/L)	Vol (mL)
Working #1			5–100	100
Stock #1	1000–20000	500		
F^-	1000		5	
Cl^-	20000		100	
Br^-	2000		10	
NO_3^- as N	2000		10	
SO_4^{2-}	20000		100	
Stock #2	1000	500		
NO_2^- as N	1000		5	
PO_4^{3-} as P	1000		5	
Working #2			2.5–50	100
Stock #1	1000–20000	250		
F^-	1000		2.5	
Cl^-	20000		50	
Br^-	2000		5	
NO_3^- as N	2000		5	
SO_4^{2-}	20000		50	
Stock #2	1000	250		
NO_2^- as N	1000		2.5	
PO_4^{3-} as P	1000		2.5	

10.2.2.3. Prepare the working standard solutions fresh daily.

10.2.3. Blanks

10.2.3.1. Calibration Blank (CB)

10.2.3.1.1. The CB consists of clean reagent water.

10.2.3.1.2. The CB is used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to

demonstrate the acceptability of the instrument baseline and to isolate the sources of contamination.

10.2.3.2. Instrument Blank (IB)

10.2.3.2.1. The IB consists of clean reagent water.

10.2.3.2.2. The IB is used to demonstrate the acceptability of the instrument baseline and to check for potential carryover or cross-contamination.

10.2.4. Calibration Standards

10.2.4.1. Prepare each calibration standard solution by diluting the appropriate volume of the working standard #1 to 10.0 mL with reagent water.

10.2.4.1.1. If the negative water peak is known to be interfering with the integration of fluoride peaks at the lower calibration levels, add 0.1 mL of the anion eluent concentrate to each calibration standard after dilution.

10.2.4.2. Use the following table as guidance to prepare the calibration standards.

Calibration Level (mg/L)			Initial		Final
			Conc (mg/L)	Vol (mL)	Vol (mL)
A1	A2	A3	A1 + A2 + A3	A1 + A2 + A3	A1 + A2 + A3
0.05	1.0	0.1	5–100	0.1	10
1.0	20	2.0	5–100	2.0	10
2.0	40	4.0	5–100	4.0	10
2.5	50	5.0	5–100	5.0	10
3.0	60	6.0	5–100	6.0	10
4.0	80	8.0	5–100	8.0	10
5.0	100	10	5–100	10	10

Note: A1 = F^-, NO_2^- as N, and PO_4^{3-} as P

A2 = Cl^- and SO_4^{2-}

A3 = Br^- and NO_3^- as N

10.2.5. Calibration Verification Standards

10.2.5.1. Use the working standard #2 as the initial calibration verification (ICV) standard solution.

10.2.5.1.1. If the negative water peak is known to be interfering with the integration of fluoride peaks, add 0.1 mL of

the anion eluent concentrate to the ICV standard after dilution.

10.2.5.1.2. The working standard used for the ICV must be of a source differing from those used for the initial calibration.

10.2.5.1.3. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard.

10.2.5.2. Prepare the continuing calibration verification (CCV) standard solution by diluting 50 mL of the working standard #1 to 100 mL with reagent water.

10.2.5.2.1. If the negative water peak is known to be interfering with the integration of fluoride peaks, add 1.0 mL of the anion eluent concentrate to the CCV standard after dilution.

10.3. Refer to Appendix A for additional reagents and standards.

10.4. All chemicals must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 500-mL pre-cleaned amber glass or high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.1.2. If MS/MSD analyses are required, collect a sufficient volume of the sample.

11.2. Solid samples should be collected in 2-oz or 4-oz pre-cleaned clear glass wide-mouth jars or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Samples shall be maintained in a chilled state, 0–6°C, not frozen, post sample collection until received at the laboratory.

11.4. Upon receipt, the samples are stored in a 0–6°C cooler.

11.4.1. Aqueous samples for nitrate, nitrite, and ortho-phosphate determinations must be analyzed within 48 hours of sample collection.

11.4.2. Aqueous samples for other anion determinations must be analyzed within 28 days of sample collection.

11.4.3. Solid samples for nitrate, nitrite, and ortho-phosphate determinations must be extracted within 7 days of sample collection, and the extracts analyzed within 48 hours post extraction.

11.4.4. Solid samples for other anion determinations must be extracted within 28 days of sample collection, and the extracts analyzed within 48 hours post extraction.

12. QUALITY CONTROL

12.1. Linear Calibration Range (LCR)

12.1.1. Following the initial instrument setup, the linearity of the calibration range for each analyte must be established prior to initial calibration.

12.1.1.1. The linearity is established for each analyte by determining the signal responses from a minimum of three different concentration standards across the range.

12.1.2. Following the establishment of a valid initial calibration, the linearity must be checked every six months, and a new LCR should be determined whenever a significant change in instrument response is observed or expected.

12.1.2.1. The linearity is checked for each analyte by determining the signal responses from a minimum of three different concentration standards across the range.

12.1.3. The linearity is deemed valid if the %D for each analyte in each check standard analyzed and quantitated against the calibration curve is ≤ 10%.

12.2. Initial Calibration (ICAL)

12.2.1. The initial seven-point calibration must be established prior to the processing of samples.

12.2.1.1. The calibration curve is established with seven calibration standards that bracket the linear calibration range of the instrument with the lowest standard being at or below the RL for each of the associated anions.

12.2.1.2. An IB shall be analyzed to demonstrate a stable baseline prior to the analysis of the calibration standards.

12.2.2. The ICAL is deemed valid if the coefficient of determination, r^2, for linear least squares regression with no weighting factor is ≥ 0.990.

12.2.3. If one or more analytes exceeds the specified control limits, employ an alternate calibration option.

12.2.3.1. The option is linear least squares regression with inverse square of concentration weighting factor. The ICAL is deemed valid if the coefficient of determination, r^2, is ≥ 0.990.

12.2.3.1.1. This option allows a better fitting of the points at the lower calibration levels.

12.2.4. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.4.1. If the problem appears to be associated with a single calibration standard, then that one standard may be re-analyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.2.4.1.1. In some cases, replace the calibration standard may be necessary.

12.2.4.2. If a calibration standard is replaced and/or re-analyzed, recalculate the correlation, and document the rationale for re-analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.

12.3.2. For EPA Method 300.0 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.3.3. For EPA Method 9056 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 5%.

12.3.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and perform one of the following tasks.

12.3.4.1. Re-analyze the ICV once immediately following the failed ICV within the same 24-hour shift.

12.3.4.2. Acquire a new ICV standard solution and analyze once immediately following the failed ICV within the same 24-hours shift.

12.3.4.3. Evaluate the instrument conditions and re-process the calibration curve data.

12.3.5. If the ICV remains unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.3.6. If the initial calibration has been verified by the ICV, sample analysis may proceed.

12.4. Initial Calibration Blank (ICB)

12.4.1. Immediately following the analysis of an ICV standard, an ICB must be analyzed prior to sample analysis.

12.4.2. The analytical system is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > MDL (or the limit specified in the project specific DQO).

12.4.3. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and re-analyze the ICB.

12.4.4. If the ICB remains unacceptable, or if the source of contamination cannot be readily identified, recalibrate.

12.5. Continuing Calibration Verification (CCV)

12.5.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence.

12.5.2. For EPA Method 300.0 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.5.3. For EPA Method 9056 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 5%.

12.5.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and perform the following tasks.

12.5.4.1. Re-analyze the CCV once immediately following the failed CCV within the same 24-hour shift.

12.5.4.2. Document the reason(s) for re-analyzing the CCV and the corrective action(s) taken.

12.5.5. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5.5.1. If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

12.5.5.2. If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

12.5.6. If the initial calibration has been verified by the CCV, sample analysis may proceed.

12.6. Continuing Calibration Blank (CCB)

12.6.1. Immediately following the analysis of a CCV standard, a CCB must be analyzed prior to sample analysis.

12.6.2. The analytical system is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > MDL (or the limit specified in the project specific DQO).

12.6.3. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and re-analyze the CCB.

12.6.4. If the CCB remains unacceptable, or if the source of contamination cannot be readily identified, recalibrate.

12.7. Reporting Limit (RL) or Limit of Quantitation (LOQ) Verification

12.7.1. For aqueous matrix, the RL (or LOQ) verification sample consists of the specified analytes spiked into clean reagent water at the RLs (or LOQs). For solid matrix, the RL (or LOQ) verification sample consists of the specified analytes spiked into washed sea sand at the RLs (or LOQs).

12.7.1.1. The RL (or LOQ) verification sample is processed in the same manner as a field sample.

12.7.2. Per client or project specific Quality Assurance Project Plan (QAPP), an RL (or LOQ) verification sample shall be prepared and analyzed immediately following the first daily calibration verification.

12.7.3. The lower and upper acceptance limits for %REC of the RL (or LOQ) verification analyte are based upon the limits outlined in the QAPP.

12.7.3.1. If the limits are not specified in the QAPP, the lower and upper acceptance limits for %REC of the RL (or LOQ) verification analyte are 50% and 150%, respectively.

12.8. Retention Time Window

12.8.1. Prior to sample analysis, establish the daily retention time window for each anion, and update the data system for proper identification.

12.8.2. Establishment of retention time window width for each analyte is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.8.2.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte) or ± T_R (where T_R is the 3S calculated from at least 30 CCV data points), whichever is greater.

Analyte	T_R (min)
Bromide	0.120
Chloride	0.060
Fluoride	0.040
Nitrate (as N)	0.140
Nitrite (as N)	0.075
o-Phosphate (as P)	0.200
Sulfate	0.250

12.8.3. Establishment of retention time window position for each analyte is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.8.3.1. When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S or ± $0.1T_R$ minute, whichever is greater.

12.8.3.2. When initial calibration is not performed, daily retention time window for each analyte is the retention time of the analyte in the CCV standard ± 3S or ± $0.1T_R$ minute, whichever is greater.

12.8.4. Retention time for each analyte in the calibration verification standard is verified as follows:

12.8.4.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 24-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.8.4.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 24-hour shift must fall within the daily retention time window established by the first CCV standard.

12.8.4.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.8.5. Occasionally, temperature fluctuation or sample matrix may create a shift in the retention time for a sample that may also impact the following CCV.

12.8.5.1. If temperature fluctuation or sample matrix is suspected, check the room temperature and re-analyze the sample to confirm that temperature fluctuation or sample matrix is the reason for the shift and not the instrument. In addition, post spiking the sample to confirm that the peak is in fact the anion in question may be warranted to properly report the analyte in a sample.

12.8.5.2. For post spike analysis, estimate the concentration in the sample and spike at a similar level. Re-analyze the post-spiked sample. If the peak is truly the anion in question, it should essentially double in height and area. If the peak appears to be split at a value greater than 20% resolution, and/or if two peaks are clearly present, then it has not been confirmed.

12.9. Event Based Quality Control (MB and LCS/LCSD)

12.9.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS), and a laboratory control sample duplicate (LCSD).

12.9.1.1. LCSD shall be prepared and processed if there is insufficient sample amount to perform the matrix based QC (i.e., MS/MSD),

or if it is mandatory per client request or project specific data quality objectives (DQOs).

12.9.1.2. QC samples shall be processed concurrently with the associated field samples. In the processing of the QC samples, the chemicals, supplies, and procedures identical to those for the field samples are used.

12.9.2. Method Blank (MB)

12.9.2.1. For aqueous matrix, the MB consists of clean reagent water. For solid matrix, the MB consists of washed sea sand.

12.9.2.2. One MB is required every day preparatory methods are performed for every batch of 20 field samples per matrix or portion thereof, whichever is more frequent.

12.9.2.3. When samples that are processed together are analyzed on different instruments or in separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. An instrument or solvent blank consisting of reagent water must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

12.9.2.4. The concentrations of target analytes in an MB should be less than the respective limits specified in the project specific DQO. In the absence of project specific DQO, the concentrations of target analytes in an MB should be less than or equal to the respective RLs. If the concentration of any target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

12.9.2.5. If a target analyte is found in the MB, refer to the current revision of SOP-T020 and the client or project specific Quality Assurance Project Plan (QAPP) for corrective action, data qualification, and reporting.

12.9.2.6. Sample results shall not be corrected for any values found in the associated MB.

12.9.3. Laboratory Control Sample (LCS/LCSD)

12.9.3.1. For aqueous matrix, the LCS consists of clean reagent water spiked with known concentrations of the specified target analytes. For solid matrix, the LCS consists of washed sea sand spiked with known concentrations of the specified target analytes.

12.9.3.2. One LCS is required every day preparatory methods are performed for every batch of 20 field samples per matrix or portion thereof, whichever is more frequent.

12.9.3.2.1. The LCSD if required is handled identically to the LCS.

12.9.3.3. The lower and upper acceptance limits for %REC of each LCS/LCSD analyte are 90% and 110%, respectively. The RPD is ≤ 15% (between LCS and LCSD).

12.9.3.4. If the %REC (and/or RPD if required) of one or more LCS (including LCSD if required) analytes are not within the acceptance limits, the preparatory and/or analytical system performance shall be suspect. Refer to the current revision of SOP-T020 and the client or project specific QAPP for corrective action, data qualification, and reporting.

12.10. Matrix Based Quality Control (MS/MSD and Sample Duplicate)

12.10.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike (MS), a matrix spike duplicate (MSD), and a sample duplicate.

12.10.1.1. A sample duplicate consists of a second aliquot of the selected field sample.

12.10.1.2. QC samples shall be processed concurrently with the associated field samples. In the processing of the QC samples, the chemicals, supplies, and procedures identical to those for the field samples are used.

12.10.2. Matrix Spike (MS/MSD)

12.10.2.1. The MS consists of the actual sample matrix spiked with known concentrations of the specified target analytes.

12.10.2.2. One MS is required every day preparatory methods are performed for every batch of 20 field samples per matrix or portion thereof, whichever is more frequent.

12.10.2.2.1. The MSD is handled identically to the MS.

12.10.2.3. The lower and upper acceptance limits for %REC of each MS/MSD analyte are 80% and 120%, respectively. The RPD is ≤ 20% (between MS and MSD).

12.10.2.4. If the %REC and/or RPD of one or more MS/MSD analytes are not within the acceptance limits, matrix effect, sample inhomogeneity, poor preparatory technique, and/or instrumentation issue shall be suspect. Refer to the current revision of SOP-T020 and the client or project specific QAPP for corrective action, data qualification, and reporting.

12.10.2.5. Unacceptable %REC is typically caused by matrix effects. Unacceptable RPD is typically caused by sample inhomogeneity. To properly evaluate the performance of the preparatory and/or analytical systems, refer to the LCS

(including LCSD if required). An acceptable LCS (and LCSD if required) usually supports matrix interference.

12.10.3. Sample Duplicate

12.10.3.1. Per EPA Method 9056 determination, client request, or project specific DQOs, one sample duplicate is required every day preparatory methods are performed for every batch of 10 field samples per matrix or portion thereof, whichever is more frequent.

12.10.3.2. The RPD is ≤ 20% (between sample and sample duplicate).

12.10.3.3. If the RPD is not within the acceptance limits, matrix effect, sample inhomogeneity, poor preparatory technique, and/or instrumentation issue shall be suspect. Refer to the current revision of SOP-T020 and the client or project specific QAPP for corrective action, data qualification, and reporting.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043.

13.3. Pipetter

13.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043.

13.4. Ion Chromatograph Initial Calibration

13.4.1. Establish an acceptable seven-point calibration curve.

13.4.1.1. Recalibration is required for changing, replacing, or reversing the analytical column.

13.4.2. After obtaining an acceptable seven-point calibration curve and prior to processing field or QC samples, an ICV standard and ICB must be analyzed to verify the initial calibration.

13.4.3. The initial seven-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.5. Retention Time Window

13.5.1. Retention time window width for each analyte is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.5.2. Document the serial number of the analytical column associated with the retention time window study.

13.5.3. Record the retention time in minutes for each analyte to three decimal places.

14. PROCEDURE

14.1. Precautions for Fluoride Determination

14.1.1. Water from filtrate injection will cause a negative peak or dip in the baseline. If fluoride elutes immediately following the negative water peak, accurate integration of the fluoride peak may be difficult at a low concentration level due to the negative water peak.

14.1.2. Reduce or eliminate the negative water peak by adding 0.1 mL of the anion eluent concentrate per 10.0 mL of each blank, standard, or sample filtrate prior to analysis.

14.1.3. If the integration issue persists for the low level fluoride peak after adding the anion eluent concentrate, apply one of the following options.

14.1.3.1. Do not report fluoride using EPA Method 300.0. Use another determinative (analytical) method such as SM 4500-F^- B/C.

14.1.3.1.1. Notify the Project Manager to obtain the client's approval prior to switching the method.

14.1.3.2. Elevate the RL to the calibration level of the initial calibration standard that can be accurately resolved. The calibration must contain a minimum of three calibration standards for this option to be acceptable.

14.1.3.2.1. Notify the Project Manager to obtain the client's approval prior to raising the RL.

14.1.3.3. Perform instrument maintenance or other corrective actions which include, but are not limited to, replacing the analytical column, changing the concentration of the eluent working solution, and/or adjusting the eluent flow rate.

14.1.3.3.1. Major change(s) to the instrument operating conditions will require the establishment of a new calibration curve, at a minimum, and possibly the establishment and verification of the method detection limit (MDL).

14.2. Sample Analysis

14.2.1. Sufficiently dilute known or suspected high concentration samples to prevent carryover or instrument contamination. Dilution of samples will result in increased reporting limits.

14.2.1.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.2.2. Use the following instrument operating parameters as guidance to establish the control program and flow rate necessary to separate the analytes of interest.

Description	Thermo Scientific Dionex ICS-1100 Operating Parameter
Pump	
Pressure – Lower Limit	200 psi
Pressure – Upper Limit	3000 psi
Eluent Flow Rate	1 mL/min
Conductivity Cell	
Temperature	30.0°C
Suppressor	
Recommended Current	53 mA
Detector	
Data Collection Rate	5.0 Hz
Gradient	
Carbonate	8.0 mM
Bicarbonate	1.0 mM
Autosampler	
Sample Loop Volume	25 µL
Delay Volume	125 µL
Delivery Speed	4.0 mL/min
Flush Factor	10

14.2.3. If the negative water peak causes an undesirable baseline, enable the "Detect Negative Peaks" parameter at the "Detection Tab" of the instrument software, and select the "Don't label" option to correct the baseline.

14.2.3.1. Refer to the online help, tutorial, and/or user manual of the Dionex Chromeleon Chromatography Management System for additional information.

14.2.4. Once established, apply the same instrument operating parameters for all subsequent blank, standard, and sample analyses.

14.3. Load the blank, standard, and sample vials onto the autosampler vial tray.

14.4. Enter the pertinent sample information, edit the sequence table, and save the sequence file in the data system.

14.4.1. If initial calibration is needed, schedule the sequence to acquire data in the following or other logical order:

1) IB
2) ICAL Standards
3) ICV Standard
4) ICB
5) RL/LOQ Verification Sample (if mandatory per QAPP)
6) QC Samples
7) Field Samples (up to 10 analyses per batch)
8) CCV
9) CCB
10) Sample Duplicate (if mandatory per QAPP)
11) Field Samples (up to 10 analyses per batch)
12) Ending CCV Standard
13) Ending CCB

14.4.2. If no initial calibration is needed, schedule the sequence to acquire data in the following or other logical order:

1) IB
2) CCV Standard
3) CCB
4) RL/LOQ Verification Sample (if mandatory per QAPP)
5) QC Samples
6) Field Samples (up to 10 analyses per batch)
7) CCV
8) CCB
9) Sample Duplicate (if mandatory per QAPP)
10) Field Samples (up to 10 analyses per batch)
11) Ending CCV Standard
12) Ending CCB

14.4.3. Instrument blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration samples), to check for potential carryover or cross-contamination.

14.5. Initiate the sequence.

14.5.1. Thoroughly document all aspects of the sample analysis in the Instrument Run Logbook.

14.6. Data Interpretation

14.6.1. Establish the daily retention time window for each analyte, and update the data system for proper identification.

14.6.2. Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window.

14.6.2.1. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 24-hour shift to evaluate retention time stability.

14.6.2.2. If any analyte in the CCV standard fall outside of its daily retention time window, refer to the client or project specific QAPP for corrective action, data qualification, and reporting.

14.6.3. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample and the calibration standards.

14.6.3.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak can be determined.

14.6.3.2. Determine the concentration based on the initial calibration curve. The data system is programmed to perform the calculation of concentration.

14.6.3.3. If the instrument response exceeds the calibration range, dilute the sample and re-analyze.

14.7. Manual Integration

14.7.1. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.7.2. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.7.3. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.7.4. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

15. CALCULATIONS

15.1. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.2. The recovery of each LCS analyte is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each MS analyte is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.5. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample or extract after dilution in mL.
V_i = volume of sample or extract before dilution in mL.

15.6. The solids content for a sample is calculated as follows:

$$C_{ss} = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where: C_{ss} = solids content in %.
M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.
M_1 = mass of weighing dish and as-received sample in g.

15.7. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = C_x \times D$$

where: C_A = concentration of target analyte in aqueous sample in mg/L.
C_x = concentration of target analyte in data system in mg/L.
D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration for a refinery aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_p \times D}{V_A}$$

where: C_A = concentration of target analyte in refinery aqueous sample in mg/L.
C_x = concentration of target analyte in data system in mg/L.
V_p = volume of refinery aqueous sample after peroxide pretreatment in mL.
Unless specified otherwise, V_p = 100.
V_A = volume of refinery aqueous sample used for peroxide pretreatment in mL.
D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in data system in mg/L.
V_{ex} = volume of extract in mL.
Unless specified otherwise, V_{ex} = 100.
W_S = mass of solid sample extracted in g.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_{ex} = concentration of target analyte in data system in mg/L.
V_{ex} = volume of extract in mL.
Unless specified otherwise, V_{ex} = 100.
W_S = mass of solid sample extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis.
If no dilution was made, D = 1.

15.11. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for soil and solid waste samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

16. METHOD PERFORMANCE

16.1. The demonstration of capability (DOC) shall be performed initially (prior to the acceptance of field samples) and when there is a significant change in instrument type, personnel, matrix, or test method.

16.2. Proficiency test (PT) sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.2.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.2.2. Extended-length protective gloves.

17.2.3. Face shield.

17.2.4. Full-length laboratory apron.

17.3. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.4. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to Quality Control (Section 12.), Data Interpretation (Section 14.6.), and the client or project specific QAPP for data assessment and acceptance criteria.

19. CORRECTIVE ACTIONS

19.1. Refer to the current revision of SOP-T022 for corrective and preventive action procedures.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the Group Leader or data reviewer of the appropriate lab group. All samples associated with an unacceptable QC set are processed according to the current revision of SOP-T020 and the client or project specific QAPP.

21. WASTE MANAGEMENT

21.1. Refer to the current revisions of SOP-T005 and SOP-T061 for the disposal of laboratory samples and waste and the treatment of wastewater.

22. REFERENCES

22.1. *Determination of Inorganic Anions by Ion Chromatography*, Approved General-Purpose Clean Water Act Analytical Methods, Method 300.0, USEPA, Revision 2.1, August 1993.

22.2. *Determination of Inorganic Anions by Ion Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1C, Method 9056, USEPA, Revision 0, September 1994.

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Update V, Volume 1B, Method 8000D, USEPA, Revision 4, July 2014.

23. APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Sample Preparation and Extraction Procedures.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

23.3. Appendix C: Control Limits for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 300.0 ***Revision 2.1*** are noted.

ECI SOP M703 Section	Reference Document EPA Method 300.0 Section	Summary of Modification
10.	7.0	Eluent and standard concentrations are modified.
Appendix A	11.7	Solid sample extraction device and time are modified.

24.2. The following modifications from EPA Method 9056 ***Revision 0*** are noted.

ECI SOP M703 Section	Reference Document EPA Method 9056 Section	Summary of Modification
10.	5.0	Eluent and standard concentrations are modified.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
5.0	All: Revise the whole SOP to reflect the current practices.	D. Tai / K. Chang	2016-03-07
5.1	Section 9.2.2: Add the new version of the instrument software application. Appendices B and C: Revise the whole appendices to conform to the DoD QSM Version 4.2.	K. Chang	2016-05-02

Appendix A

SAMPLE PREPARATION AND EXTRACTION PROCEDURES

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 300.0/9056, Determination of Inorganic Anions by Ion Chromatography – Sample Preparation and Extraction Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts or technicians experienced in the use of the equipment and apparatus required to execute the procedure.

3. INTERFERENCES

3.1. Samples that contain particles larger than 0.45 µm, and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

3.2. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample should be purged with an inert gas (argon or nitrogen) for approximately 5 minutes or until no chlorine dioxide remains.

4. EQUIPMENT AND SUPPLIES

4.1. Test tubes, 17-mm × 100-mm (16.0-mL), polystyrene, disposable.

4.2. Beakers, 50-mL, 100-mL, 500-mL, or other capacity, glass.

4.3. Erlenmeyer flasks, 125-mL or other capacity, glass.

4.4. Spatula, stainless steel.

4.5. Syringe filtration apparatus:

4.5.1. Syringe, 10-mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

4.5.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing, disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

4.5.3. Filter, 0.22-µm effective pore size, 33-mm diameter, non-sterile, hydrophilic, polyvinylidene fluoride (PVDF) membrane, polypropylene housing, disposable, EMD Millipore Millex-GV Syringe Filter SLGV033NK or equivalent.

4.6. Purging apparatus:

4.6.1. Round bottom flask, 1-L or other capacity, 19/38 joint size, two necks, borosilicate glass.

4.6.2. Support stand, cast-iron, equipped with adjustable angle clamps.

4.6.3. Nitrogen, N_2, 99.998%, compressed, Praxair 4.8 grade or higher.

4.7. Centrifuge, 250–6000-rpm variable speed, 1–30-min digital timer, VWR International Clinical 200 Large Capacity Centrifuge or equivalent.

4.8. Ultrasonic bath, VWR Scientific Aquasonic Model 550T Ultrasonic Cleaner or equivalent.

4.9. Parafilm, thermoplastic, Parafilm M® Laboratory Film or equivalent.

4.10. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

4.11. Refer to the standard procedure for additional equipment and supplies.

4.12. All critical supplies and consumable materials that have the potential of introducing contaminants must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

4.12.1. The critical supplies and consumable materials for this procedure are test tubes, autosampler vials, syringes, and filters.

5. REAGENTS AND STANDARDS

5.1. Reagents

5.1.1. Lead acetate test strips, white color paper.

5.1.1.1. The lead acetate test paper turns black in the presence of hydrogen sulfide and other soluble sulfides.

5.1.2. Hydrogen peroxide, H_2O_2, 30% (v/v), clear colorless liquid, certified, reagent grade or equivalent.

5.1.2.1. Prepare the anion eluent concentrate by dissolving 21.198 g of Na_2CO_3 and 2.1002 g of $NaHCO_3$ in reagent water and dilute to 250 mL with additional reagent water.

5.2. Standards

5.2.1. Spike Standards

5.2.1.1. Use the second source stock standards #1 and #2 as the spike working standards #1 and #2, respectively.

5.2.1.2. Prepare the quality control (QC) samples (i.e., LCS/LCSD and MS/MSD) by adding the appropriate volumes of the spike working standards to each QC sample prior to aqueous sample analysis or solid sample extraction.

5.3. Refer to the standard procedure for additional reagents and standards.

5.4. All chemicals must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

6. CALIBRATION AND STANDARDIZATION

6.1. Top Loading Balance

6.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

6.1.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

6.2. Refer to the standard procedure for additional information on calibration and standardization.

7. PROCEDURE

7.1. Aqueous Sample Preparation

7.1.1. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

7.1.1.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10−20 minutes.

7.1.2. Measure at least 10.0 mL of the aqueous sample into a clean test tube. Record the test tube identification number.

7.1.2.1. For MB/LCS/LCSD, measure exactly 10.0 mL of clean reagent water.

7.1.2.2. For MS/MSD, measure exactly 10.0 mL of the aqueous sample in each analytical batch selected for spiking. Record the sample identification number.

7.1.3. Add 25 µL of each spike working standard to each LCS, LCSD (if required), MS, and MSD.

7.1.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 25 µL of the spike working standard #1 to each LCS, LCSD (if required), MS, and MSD.

7.1.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 25 µL of the spike working standard #2 to each LCS, LCSD (if required), MS, and MSD.

7.1.4. Proceed to Section 7.7. of this appendix for filtration.

7.2. Refinery Aqueous Sample Preparation

7.2.1. Allow a refinery aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the refinery aqueous sample to settle.

7.2.1.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10−20 minutes.

7.2.2. Measure exactly 10.0 mL of the aqueous sample into a clean round bottom flask.

7.2.2.1. For MB/LCS/LCSD, measure exactly 10.0 mL of clean reagent water.

7.2.2.2. For MS/MSD, measure exactly 10.0 mL of the refinery aqueous sample in each analytical batch selected for spiking. Record the sample identification number.

7.2.3. Add 250 µL of each spike working standard to each LCS, LCSD (if required), MS, and MSD.

7.2.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 250 µL of the spike working standard #1 to each LCS, LCSD (if required), MS, and MSD.

7.2.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 250 µL of the spike working standard #2 to each LCS, LCSD (if required), MS, and MSD.

7.2.4. Add 90 mL of reagent water and 1.0 mL of 30% hydrogen peroxide to the round bottom flask.

7.2.4.1. Yellow color in the solution indicates the presence of sulfide.

7.2.5. Assemble the purging apparatus and purge the diluted sample with nitrogen for a minimum of 12 hours or until the solution remains colorless.

7.2.5.1. If the yellow color persists, add 5 drops of 30% hydrogen peroxide periodically (i.e., every 2−4 hours), and continue purging until the solution remains colorless.

7.2.6. Verify the absence of sulfide by transferring a drop of the purged sample onto a lead acetate test strip. A white color indicates the absence of sulfide, and a black color indicates the presence of sulfide.

7.2.6.1. If sulfide is still present, add 5 drops of 30% hydrogen peroxide periodically (i.e., every 2−4 hours), and continue purging until sulfide is completely removed.

7.2.7. Transfer the purged sample into a clean specimen container, and adjust the volume to 100 mL with reagent water. Record the specimen container identification number.

7.2.8. Cap the specimen container and shake to mix the purged sample.

7.2.9. Proceed to Section 7.7. of this appendix for filtration.

7.3. Solid Sample Preparation

7.3.1. Homogenize a solid, soil, or sediment sample as outlined in the current revision of SOP-M230.

7.3.2. Measure 10.0 ± 0.1 g (wet weight) of the homogenized solid sample into a clean specimen container. Record the specimen container identification number.

7.3.2.1. For MB/LCS/LCSD, measure 10.0 ± 0.1 g (wet weight) of washed sea sand. Record the washed sea sand identification number.

7.3.2.2. For MS/MSD, measure 10.0 ± 0.1 g (wet weight) of the solid sample in each analytical batch selected for spiking. Record the sample identification number.

7.3.3. Add 250 µL of each spike working standard to each LCS, LCSD (if required), MS, and MSD.

7.3.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 250 µL of the spike working standard #1 to each LCS, LCSD (if required), MS, and MSD.

7.3.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 250 µL of the spike working standard #2 to each LCS, LCSD (if required), MS, and MSD.

7.3.4. Add 100 mL of reagent water to the specimen container.

7.3.5. Cap the specimen container and shake to mix the slurry.

7.3.6. Place the specimen container in the ultrasonic bath and sonicate the slurry for 30 minutes at ambient temperature.

7.3.6.1. The aqueous phase of the slurry is the solid sample extract.

7.3.7. Allow the solid phase and the suspended particulates, if any, in the extract to settle.

7.3.7.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10−20 minutes.

7.3.8. Proceed to Section 7.7. of this appendix for filtration.

7.4. Aqueous RL (or LOQ) Verification Sample Preparation

7.4.1. Measure the appropriate volume of each stock standard into a clean 100-mL volumetric flask and dilute to 100 mL with reagent water. The concentration of each analyte shall be at its RL (or LOQ).

7.4.2. Cap the volumetric flask and invert a minimum of three times to mix thoroughly.

7.4.3. Measure at least 10.0 mL of the RL (or LOQ) verification sample into a clean test tube. Record the test tube identification number.

7.4.4. Proceed to Section 7.7. of this appendix for filtration.

7.5. Refinery Aqueous RL (or LOQ) Verification Sample Preparation

7.5.1. Measure the appropriate volume of each stock standard into a clean 100-mL volumetric flask and dilute to 100 mL with reagent water. The concentration of each analyte shall be at its RL (or LOQ).

7.5.2. Cap the volumetric flask and invert a minimum of three times to mix thoroughly.

7.5.3. Measure exactly 10.0 mL of the RL (or LOQ) verification sample into a clean round bottom flask.

7.5.4. Proceed to Section 7.2.4. of this appendix for sulfide removal.

7.6. Solid RL (or LOQ) Verification Sample Preparation

7.6.1. Measure 10.0 ± 0.1 g (wet weight) of washed sea sand into a clean specimen container. Record the specimen container and the washed sea sand identification numbers.

7.6.2. Measure the appropriate volume of each stock standard into the same specimen container and add 100 mL of reagent water. The concentration of each analyte shall be at its RL (or LOQ).

7.6.3. Cap the specimen container and shake to mix the slurry.

7.6.4. Proceed to Section 7.3.6. of this appendix for extraction.

7.7. Sample Filtration

7.7.1. Pull the plunger of a syringe and draw the sample or extract into the barrel. Record the syringe identification number.

7.7.2. Attach a clean 0.45-µm membrane filter and press the plunger to filter the sample or extract. Discard the first few drops of the filtrate. Record the membrane filter identification number.

7.7.2.1. Slowly push down on the plunger until the sample or extract begins to pass through the filter. Do not use excessive force as the filter may rupture.

7.7.3. Collect approximately 10 mL of the sample filtrate in a clean test tube and label appropriately. Record the test tube identification number.

7.7.4. If the filtrate appears to be turbid or colored, assemble the syringe filtration apparatus with a clean 0.22-µm membrane filter. Filter and collect the filtrate. Record the membrane filter identification number.

7.7.5. If water dip is known to be interfering with the integration of fluoride peaks at lower concentration levels, add 0.1 mL of the anion eluent concentrate per 10.0-mL aliquot of each blank, standard, and sample filtrate.

7.7.6. Cover the test tube with parafilm.

7.7.7. Transfer an aliquot of the filtrate into a clean autosampler vial immediately prior to analysis.

7.7.8. Process all QC samples and extracts in the same manner.

7.7.9. Thoroughly document all aspects of the sample preparation in the Anion Sample Preparation Logbook.

7.7.10. Proceed to analysis.

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 9056, Determination of Inorganic Anions by Ion Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. ►STANDARDS

4.1. Initial Calibration Verification (ICV)

4.1.1. The concentration of the ICV standard shall be at or near the midpoint of the calibration range.

4.2. Continuing Calibration Verification (CCV)

4.2.1. The concentration of the CCV standard shall be ***between*** the low calibration standard and the midpoint of the calibration range.

4.3. The use of a standard from a second lot ***as a second source standard is acceptable when only one manufacturer of the standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.***

5. ►QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. Detection limit (DL) determination shall be performed for each analyte at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following each DL determination and quarterly thereafter.

5.1.2.1. LOD verification sample shall be prepared by spiking a quality system matrix at ***approximately 2 to 3 times the DL (for a single-analyte standard) or greater than 1 to 4 times the DL (for a multi-analyte standard).***

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise (S/N) ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., retention time, pattern recognition, etc.).

5.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the DL determination and LOD verification ***at a higher concentration***.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the calibration range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ for each analyte.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking a quality system matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The LOQ and the highest calibration standard establish the quantitation range.

5.3.1.1. When sample results exceed the quantitation range, dilute and re-analyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.

5.4. Initial Calibration Verification (ICV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

5.5. Continuing Calibration Verification (CCV)

5.5.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

5.5.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. ***Effect corrective action and re-analyze the CCV.***

5.5.2.1. If the ***CCV remains unacceptable***, recalibrate and re-analyze all samples since the last acceptable CCV.

5.6. Retention Time Window

5.6.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

5.6.1.1. When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S.

5.6.1.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte is the retention time of the analyte in the CCV standard ± 3S.

5.7. Event Based Quality Control (MB and LCS/LCSD)

5.7.1. Method Blank (MB)

5.7.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.7.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the ***RL***, <u>and</u> is greater than 1/10 the amount measured in any associated sample or 1/10 the regulatory limit (whichever is greater).

5.7.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds ***RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater)***.

5.7.1.1.3. ***The MB result is otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).***

5.7.1.2. If the MB is contaminated, re-process the affected samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.7.1.2.1. If insufficient sample volume remains for re-processing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.7.2. Laboratory Control Sample (LCS/LCSD)

5.7.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD analyte in aqueous and solid matrices are listed in Appendix C.

5.7.2.2. All reported analytes must be spiked. The concentration of each spike analyte shall be at or below the midpoint of the calibration if project specific concentration is not specified.

5.7.2.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2.3.1. ***Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.***

5.7.2.4. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.8. Matrix Based Quality Control (MS/MSD and Sample Duplicate)

5.8.1. Matrix Spike (MS/MSD)

5.8.1.1. The lower and upper acceptance limits for %REC of each MS/MSD analyte in aqueous and solid matrices are listed in Appendix C. The RPD is ≤ 15% (between MS and MSD).

5.8.1.2. All reported analytes must be spiked. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5.8.1.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.8.1.3.1. ***Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.***

5.8.2. Sample Duplicate

5.8.2.1. The RPD is ≤ 15% (between sample and sample duplicate).

6. REFERENCES

6.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version ***4.2, October 2010***.

Appendix C

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD

Water Matrix		
	Control Limit	
Analyte	Lower	Upper
Bromide	80	120
Chloride	80	120
Fluoride	80	120
Nitrate (as N)	80	120
Nitrite (as N)	80	120
Phosphate (as P)	80	120
Sulfate	80	120

Soil Matrix		
	Control Limit	
Analyte	Lower	Upper
Bromide	80	120
Chloride	80	120
Fluoride	80	120
Nitrate (as N)	80	120
Nitrite (as N)	80	120
Phosphate (as P)	80	120
Sulfate	80	120

Title : **EPA METHOD 314.0, PERCHLORATE BY ION CHROMATOGRAPHY**

Document No. : SOP-M709
Revision No. : 3.0
Supersedes : 2.4

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PROPRIETARY INFORMATION STATEMENT

Revision 3.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 09/23/15
MANAGEMENT **DATE**

_____ 09-23-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 314.0, Perchlorate by Ion Chromatography.

2. APPLICABLE MATRICES

2.1. Drinking, reagent, surface and ground waters.

2.2. Soil, solid and non-aqueous matrices may be analyzed using the extraction procedure noted in Appendix A and reporting as a modified method, EPA Method 314.0(M).

3. ►DETECTION / QUANTITATION LIMITS

3.1. The nominal reporting limit (RL) for aqueous samples is 2.0 µg/L. Soil/Solid matrices are reported at 20 µg/kg.

3.2. The RL will be proportionately higher for samples that require dilutions.

3.2.1. In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained, and must be capable of yielding a baseline with no more than 5 nanoSiemens (nS) noise/drift per minute of monitored response over the background conductivity.

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. EPA Method 314.0 describes chromatographic procedures that will allow for the separation of perchlorate and its quantitative analysis by IC. Detection is achieved using a conductivity detector.

4.2. Method 314.0 is used to determine perchlorate concentrations in drinking water and similarly "clean" water samples. The method may also be applied to reagent, surface and ground waters.

4.3. Method 314.0M is used to determine perchlorate concentrations in soil and solid matrices. Reference Appendix A for soil / solid specific procedures.

4.4. This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography (IC) and skillful in the interpretation of chromatographic data.

5. METHOD SUMMARY

5.1. Volume of 1250 µL of a sample is introduced to an IC. The IC is comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column,

suppressor device, and conductivity detector. Perchlorate is separated and measured as it passes these systems.

6. ►DEFINITIONS

6.1. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.1.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.1.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.2. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised.

6.3. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.4. Matrix Spike (spiked sample, fortified sample, or laboratory fortified sample matrix): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.5. Matrix Spike Duplicate (spiked sample duplicate, fortified sample duplicate, or laboratory fortified sample matrix duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.6. Method Blank (laboratory reagent blank): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.7. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.8. Terms Specific to IC Analysis

6.8.1. Initial Calibration Check Standard (ICCS): A CAL solution that is analyzed initially, prior to any field sample analyses, which verifies the previously established calibration curve. The concentration for the initial calibration check standard MUST be at or below the MRL level.

6.8.2. Continuing Calibration Check Standard (CCCS): A CAL solution which is analyzed after every tenth field sample analyses, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous ten field samples analyzed. The concentration for the continuing calibration check standard should be either at a middle calibration level or at the highest calibration level (Section 13.3.2.).

6.8.3. End Calibration Check Standard (ECCS): A CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curve and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard (Section 13.3.2.). The ECCS is not of the same concentration used for the CCCS.

6.8.4. Instrument Performance Check Solution (IPC): A solution containing a specific concentration of perchlorate and other test substances (namely chloride, sulfate and carbonate) used to evaluate the performance of the instrument system with respect to a defined set of criteria.

6.8.5. Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.8.6. Lower limit of quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.

6.8.7. Matrix Conductivity Threshold (MCT): The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution or pretreatment is required. The conductance of a sample matrix is proportional to the common anions present in the matrix (which contributes to the level of total dissolved solids [TDS]) which can greatly affect the integrity of this analysis. The value for this threshold is dependent on the conditions, hardware, and state of the hardware employed. Consequently, this threshold is not method-defined and must be determined by the individual analytical

laboratory during the Initial Demonstration of Capability (IDC) and confirmed in each analysis batch using the Instrument Performance Check (IPC) solution. Matrix conductivity is measured in microSiemens/cm (µS/cm) or microMhos/cm (µMhos/cm) which are considered equivalent terms.

6.8.8. Peak Area to Height Ratio (A/H): The ratio of the peak area divided by the peak height is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT, and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.

6.8.9. Quality Control Sample (QCS): A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

6.8.10. Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration.

6.9. Please refer to the current version of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.

7. INTERFERENCES

7.1. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.

7.2. Interferences can be divided into three different categories:

7.2.1. Direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion.

7.2.2. Concentration dependent coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlaps into the retention window of the target anion.

7.2.3. Ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

7.2.4. A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst MUST verify that these changes do not induce any negative effects on method performance by repeating and passing all the QC criteria as described in Section 12.

7.2.5. Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependent coelution or ionic character displacement, but it must be clarified that sample dilution will alter your Minimum Reporting Limit (MRL) by proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution may be dilution of the eluent as outlined in Section 14.2.6.

7.2.6. Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. With any proposed pretreatment, the analyst must verify that the target analyte is not affected by monitoring recovery after pretreatment (additional pretreated LCS requirement see Sections 12.3.3.1. and 14.1.5.2.) and that no background contaminants are introduced by the pretreatment (additional pretreated MB requirement see Sections 12.3.1.1. and 14.1.5.2.). With advances in analytical separator column technology that employ higher capacity anion exchange resins, the need for these cartridges has been greatly reduced.

7.2.6.1. Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges that can foul the guard and analytical columns, causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) or use calibration chromatograms generated when the column was initially installed, to ensure proper separation and similar response ratios between the target analytes are observed.

7.2.6.2. If MB background problems are encountered in the retention time window for perchlorate when these pretreatment cartridges have been employed, increase the initial reagent water rinse of the cartridge to approximately five times the volume specified by the manufacturer.

7.3. Sample matrices with high concentrations of common anions such as chloride, sulfate, and carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing a protracted tailing following the initial elution of the more weakly retained anions (chloride, carbonate, and sulfate) which extends into the perchlorate retention time window. Monitoring the conductivity (Calscience SOP-M702) of the matrix can indirectly assess these common anion levels. Consequently, all sample matrices

must be monitored for conductivity prior to analysis. When the laboratory determined Matrix Conductivity Threshold (MCT, see Section 12.2.8.) is exceeded, procedures incorporating sample dilution and/or pretreatment must be performed as specified in Sections 14.1.4. and 14.1.5., respectively. The sample(s) must first be processed as a diluted sample(s) prior to pre-treatment. If the diluted sample is Not Detected (ND) at the higher Reporting Level (RL) and after consultation with the client to authorize additional measures, then pre-treatment processing with the appropriate cartridge may be done to bring the original sample within the MCT range without dilution. Project specific requests may supercede this decision process.

7.4. Sample filtration must be employed on every sample prior to analysis, using a filter no larger than a 0.45-µm nominal pore size membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. This applies not only to field samples but also to the laboratory method blank (MB) and laboratory control sample (LCS). The MB and LCS samples function as controls and must be filtered to confirm no bias is attributable to the filtration. Filter the samples through a membrane or frit with no larger than a 0.45-µm nominal pore size. Syringe mounted, cartridge filters work well. Filters specifically designed for IC applications should be used.

7.5. Close attention should be given to the potential for carry over peaks from one analysis that will affect the proper detection of perchlorate in a second, subsequent analysis. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

8. SAFETY

8.1. The following chemicals have the potential to be highly toxic or hazardous (consult SDSs).

8.1.1. Sodium hydroxide (NaOH) used in the preparation of the eluent is considered caustic.

8.2. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

8.3. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling samples and chemicals.

8.4. Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the SDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Ion chromatograph (IC), Dionex DX-320 or equivalent: Analytical system complete with eluent reservoirs, and ion chromatographic pump, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system.

9.1.1. Anion guard column: Dionex AG16, 4-mm (P/N 055377) or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.

9.1.2. Anion separator column: Dionex AS16, 4-mm (P/N 055376) or equivalent.

9.1.2.1. The AG16/AS16 columns can tolerate much higher levels of these common anions and therefore, it is recommended in this method as the column of choice.

9.1.2.2. Any alternate, equivalent column must be characterized as hydrophilic or conversely, must be rated as having low to very low hydrophobicity. This is one characteristic that is consistent for the AS5, AS11 and AS16 analytical separator columns. This requirement for low hydrophobicity is to allow the efficient, reproducible and symmetrical band elution of polarizable anions, such as perchlorate. If the perchlorate analysis is attempted on a hydrophobic column, such as those typically used for the analysis of common anions, poor performance will result due to very asymmetric, tailing peaks. Conduct a typical analysis using a middle to high calibration standard. Any alternate column must be capable of yielding symmetrical peak elution for this perchlorate response as demonstrated by yielding a Peak Gaussian Factor ***(PGF)*** of between 0.80 and 1.15 using the following equation.

$$PGF = \frac{1.83 \times W_{(1/2)}}{W_{(1/10)}}$$

Where: $W_{(1/2)}$ = the peak width at half height
$W_{(1/10)}$ = the peak width at tenth height

Note: Values for $W_{(1/2)}$ and $W_{(1/10)}$ can be attained through most data acquisition software.

9.1.3. Anion suppressor device: The data presented in this method are generated using a Dionex Anion Self-Regenerating Suppressor (ASRS ULTRA II, 4-mm, P/N 061561). An equivalent suppressor device may be utilized provided comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS/min over the background conductivity. Proper suppressor performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

9.1.4. Detector: Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Section 12.2.

9.2. Instrument Software

9.2.1. Requires a PC based data system or equivalent.

9.2.2. Dionex Chromeleon 6.6 or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. Conductivity Meter: Used to monitor sample matrix conductance that is directly related to the common anion levels in a matrix and is used to determine if sample pretreatment is required. At a minimum, this meter should be capable of measuring matrix conductance over a range of 1 to 10000 µS/cm.

9.5. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg. Used to accurately weigh target analyte salt for stock standard preparation.

9.6. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g. Used to accurately weigh reagents such as sodium hydroxide solution in the preparation of eluents.

9.7. Weigh Boats: Plastic, disposable; used for weighing eluent reagents.

9.8. Micro Beakers: Plastic, disposable; used during sample preparation.

9.9. Syringes: Plastic, disposable, 10-mL; used during sample preparation.

9.10. Pipettes: Pasteur, plastic or glass, disposable, graduated, 5-mL and 10-mL.

9.11. Volumetric flasks: glass, 100-mL.

9.12. Bottles: High-density polyethylene (HDPE) or glass, amber or clear, 30-mL, 125-mL, 250-mL. For sampling and storage of calibration solutions. Stability studies presented by the Interagency Perchlorate Steering Committee for Analytical Methods and confirmed at the EPA, indicated perchlorate is neither photoreactive nor prone to adsorption to the walls of either HDPE plastic or glass bottles.

9.13. Particulate Filters: 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, P/N 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.

9.14. Matrix pretreatment cartridges in divinylbenzene: (Dionex OnGuard II RP cartridges, P/N 057083, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of humic acids and fulvic acids.

9.15. Matrix pretreatment cartridges in the barium form: (Dionex OnGuard II Ba cartridges, P/N 057093, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of sulfate.

9.16. Matrix pretreatment cartridges in the silver form: (Dionex OnGuard II Ag cartridges, P/N 057089, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of chloride.

9.17. Matrix pretreatment cartridges in the hydrogen form: (Dionex OnGuard II H cartridges, P/N 057085, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce cations in the sample matrix. This protects the analytical column by removing silver or barium that has leached from the Ag or Ba cartridges and may indirectly minimize the effect of carbonate by removing the cationic counter ion.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water: Distilled or deionized water 17.8-Mohm or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

10.1.2. Eluent solution: 50-mM sodium hydroxide (NaOH, [CASRN 1310-73-2]), dissolve 2.0 g of NaOH in reagent water to a final volume of 1.0 L. Alternatively, measure 2.6 mL of 50% (W/W) NaOH solution with a 5-mL pipette, and dilute in reagent water to a final volume of 1.0 L.

10.1.2.1. Solutions of NaOH are very susceptible to carbonate contamination resulting from adsorption of carbon dioxide from the atmosphere. This contamination will result in poor reproducibility of perchlorate retention times, elevated instrument background conductivity, and increased baseline noise/drift. Consequently, exposure to the atmosphere should be minimized by storing these eluent solutions in sealed reservoirs under low pressure (3 to 5 psi) helium. In addition, these solutions should be regularly prepared and held for no more than 5 days. When refilling the eluent reservoir, completely replace the old eluent solution by emptying the old eluent, rinsing the reservoir with reagent water, and refilling with the freshly prepared eluent solution. With this eluent, the suppressed conductivity detector background signal should be less than 3 µS, based upon manufacturer's guidelines.

10.1.2.2. This eluent solution must be purged for 10 minutes with helium prior to use. This effectively removes dissolved gases that may form micro bubbles in the IC, compromising system performance and adversely affecting the integrity of the data. Alternatively, an in-line degas apparatus may be employed.

10.1.2.3. A system or apparatus that automatically generates the hydroxide eluent (Dionex EG40, or equivalent) is an acceptable alternative to physically preparing this hydroxide eluent.

10.1.3. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Perchlorate stock standard solution, 1000-mg/L (1-mg/mL): A stock standard solution may be purchased as a certified solution or prepared from ACS reagent grade, sodium salt as listed below.

10.2.1.1. NOTE: Sodium perchlorate represents a molar weight fraction of 81.2% perchlorate anion.

10.2.1.2. Perchlorate (ClO_4^-) 1000-mg/L: Dissolve 1.2312-g sodium perchlorate ($NaClO_4$, CASRN [7601-89-0]) in reagent water and dilute to a final volume of 1.0 L.

10.2.1.2.1. ***Alternatively, the standard(s) may be prepared gravimetrically by weighing the appropriate masses of the salts into a specimen cup and bringing to final volume with a calibrated pipetter.***

10.2.1.3. Stability of standards: Perchlorate stock standards, stored at room temperature, appear to be very stable and may be stable for an extended period of time. However, specified expiration dates should be marked on each prepared stock standard as part of any laboratory's quality control program. In this regard, it is recommended that stock standards for perchlorate are held for no more than 12 months and an expiration date should be clearly specified on the label.

10.2.2. Mixed Common Anion Stock Solution: Containing the anions chloride, sulfate and carbonate each at 25-mg/mL anion concentration. This solution is used to prepare simulated common anion sample in the determination of the MCT.

10.2.2.1. Dissolve the following salts in reagent water to a final volume of 100 mL:

10.2.2.1.1. 4.0-g sodium chloride (NaCl, CASRN [7647-14-5]) = 2.4-g Cl^-

10.2.2.1.2. 3.7-g sodium sulfate (Na_2SO_4, CASRN [7757-82-6]) = 2.5-g SO_4^{2-}

10.2.2.1.3. 4.4-g sodium carbonate (Na_2CO_3, CASRN [497-19-8]) = 2.5-g CO_3^{2-}

10.2.3. Conductivity Meter Calibration Solution. The conductivity calibration solution is purchased, ready to use.

10.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Samples may be collected in 125-mL / 100-mL sterile high density polyethylene (HDPE) containers with Teflon-lined closures. All bottles must be cleaned and certified by the manufacturer or supplier. The volume collected should be sufficient to ensure a representative sample, allow for replicated analysis and laboratory matrix spike analysis, if required, and minimize waste disposal.

11.2. No preservation chemicals are required.

11.3. Samples should be maintained in a chilled state post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3.1. For additional information on aqueous and non-aqueous (except tissue) sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).

11.4. Upon receipt, the samples are stored in a 0~6°C cooler. Samples should be analyzed within 28 days of collection.

12. ►QUALITY CONTROL

12.1. Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory capability, and subsequent analysis in each analysis batch (Section 6.1.) of a Quality Control Sample (QCS), Instrument Performance Check Standard (IPC), Laboratory Method Blank (MB), Initial Calibration Check Standard (ICCS), Laboratory Control Sample (LCS), Continuing and End Calibration Check Standards (CCCS/ECCS), Laboratory Matrix Spike (MS) and either a Laboratory or MS duplicate sample analysis. This section details the specific requirements for each of these QC parameters. The laboratory is required to maintain performance records that define the quality of the data that are generated.

12.2. Initial Demonstration of Capability

12.2.1. The initial demonstration of capability (IDC) is used to characterize instrument and laboratory performance prior to performing analyses by this method.

12.2.2. Initial demonstration of low system background: See Section 12.3.1.

12.2.3. Initial Demonstration of Accuracy (IDA): Prepare and analyze 7 replicate LCSs fortified at 25.0 µg/L. Calculate the mean measured concentration $(C_{\bar{x}})$ of the replicate values as follows.

$$C_{\bar{x}} = \frac{(C_1 + C_2 + C_3 + \cdots + C_n)}{n}$$

where,

$C_{\bar{x}}$ = mean recovered concentration of the replicate analysis.

$C_1, C_2, \ldots, C_n$ = recovered concentrations of the replicate 1, 2, ..., n.

n = 7

To pass the IDA, the value derived for $C_{\bar{x}}$ must be within ± 10% of the true value or between 22.5 µg/L and 27.5 µg/L.

12.2.4. Initial Demonstration of Precision (IDP): Using the data generated for Section 12.2.3., calculate the percent relative standard deviation (%RSD) of the replicate analysis, as indicated below. To pass the IDP, the %RSD must be less than 10%.

$$\%RSD = \frac{S_{n-1}}{C_{\bar{x}}} \times 100$$

where,

S_{n-1} = sample standard deviation $(n-1)$ of the replicate analyses.

$C_{\bar{x}}$ = mean recovered concentration of the replicate analysis.

12.2.5. Quality Control Sample (QCS): After calibration curves have initially been established or have been re-established, or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source QCS. If the determined concentrations are not within ± 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the IDC or continuing with on-going analyses.

12.2.6. Method Detection Limit (MDL): An MDL must be established using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over a three-day period. These seven MDL replicate analyses may be performed gradually over three days or may represent data that has been collected, at a consistent MDL estimated concentration, over a series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times S_{n-1}$$

where,

t = student's t value for a 99% confidence level and a standard deviation estimate with $(n-1)$ degrees of freedom [t = 3.14 for seven replicates].

S_{n-1} = sample standard deviation $(n-1)$ of the seven replicate analyses.

12.2.6.1. MDLs should be periodically verified, but must be initially determined when a new operator begins work or whenever there is a significant change in the background, or instrument response.

NOTE: Do not subtract blank values when performing MDL calculations.

12.2.7. Minimum Reporting Level (MRL): The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration that would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated QC failure upon analysis of the ICCS. Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard.

12.2.8. Matrix Conductivity Threshold (MCT): The MCT is an individual laboratory defined value that must be determined by preparing a series of sequentially increasing, common anion fortified, reagent water samples each contain a constant perchlorate concentration. Initially, reagent water prepared LCS, containing no common anions, must be analyzed which contains perchlorate at a suggested concentration of 25-µg/L perchlorate. Next, the series of sequentially increasing concentrations of 50, 100, 200, 400, 600, 800, and 1000 mg/L for each anion. A concentration of 25-µg/L perchlorate has been suggested, assuming the MRL has been set in the range of 3.0 µg/L to 5.0 µg/L. If a laboratory's MRL is higher, choose a perchlorate concentration for this exercise at approximately 5 times the MRL.

12.2.8.1. Prepare the mixed common anion stock solution containing chloride, sulfate and carbonate, each at 25 mg/mL.

12.2.8.2. Prepare a perchlorate secondary stock dilution standard at 10 mg/L from the 1000-mg/L perchlorate stock standard by diluting 1.0 mL of the stock solution to a final volume of 100 mL.

12.2.8.3. Prepare the LCS at suggested perchlorate concentration of 25 µg/L by diluting 0.25 mL of the perchlorate secondary stock dilution standard to a final volume of 100 mL.

12.2.8.4. Next, prepare the series of common anion fortified reagent water samples by adding 0.20 mL, 0.40 mL, 0.80 mL, 1.6 mL, 2.4 mL, 3.2 mL, and 4.0 mL of the mixed common anion stock solution (Section 10.4.) into separate 100-mL volumetric flasks. Next, add 0.25 mL of the perchlorate secondary stock dilution

standard to each 100-mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25.0 µg/L.

12.2.8.5. Measure and record the conductance of each of these prepared solutions on a calibrated conductivity meter (This meter must be calibrated as described in Section 13.4 prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride at 400 mg/L, sulfate at 400 mg/L, and carbonate at 400 mg/L, should display a conductance of between 3200 µS/cm and 3700 µS/cm.

12.2.8.6. Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate. In many data acquisition and instrument control software, the peak area to height ratio is a definable parameter that can be specified for printout on the analysis report.

12.2.8.7. Both the A/H ratio and quantified perchlorate concentration for the LCS and the 200-mg/L mixed common anion solution should be reproducibly consistent but as the common anion levels increase, the A/H ratio will also begin to increase as the peak height is distorted and reduced. As the peak is distorted, the area will also eventually begin to be distorted and the quantitated concentration will be reduced, but this is typically secondary, with the ratio of the peak area to height initially predicting this pending quantitation problem.

12.2.8.8. Calculate the A/H ratio percent difference ($PD_{A/H}$) between the average A/H ratio for the LCS (A/H_{LCS}) and the average A/H ratios for each mixed common anion solutions (A/H_{MA}) using the following equation.

$$PD_{A/H} = \frac{|A/H_{LCS} - A/H_{MA}|}{A/H_{LCS}} \times 100$$

12.2.8.9. As the conductivity of the matrices increases, the $PD_{A/H}$ will increase. The MCT is the matrix conductance where the $PD_{A/H}$ exceeds 20%. To derive the MCT, perform a linear regression on these data by plotting $PD_{A/H}$ (as the independent variable, x) versus the matrix conductance (as the dependent variable, y). The resulting regression data should yield a r^2 value of >0.95. Record the "constant" (intercept value) and the "X-coefficient" (slope), and calculate the MCT as:

$$MCT = (20\%) \times (X - coefficient) + (constant)$$

NOTE: Be careful to consistently apply percentages as either whole numbers or as fractional values (20% = 0.20) for both the regression analysis and the MCT calculation.

12.2.8.10. As an alternate to the regression analysis, the laboratory can choose to establish their MCT at the conductance level of the highest mixed anion solution that yielded a $PD_{A/H}$ value below the 20% threshold.

12.2.8.11. As a final procedure, the laboratory should confirm their perchlorate MRL in a mixed common anion solution that reflects a conductance near (within ± 10%) that is specified as the MCT. This solution must contain perchlorate, at the laboratory determined MRL, as well as the common anions chloride, sulfate and carbonate. It is prepared by adding the appropriate volume (0.5 - 3.0 ml) of the mixed common anion stock solution based upon the each instrument's calculated MCT and 20 µL of the perchlorate secondary stock dilution standard to a 100-mL volumetric flask. This is diluted to a final volume of 100 mL with reagent water (such that the perchlorate concentration is 2.0 µg/L). The conductance of this solution must be measured at within ± 10% of the MCT and following the analysis, the recovered perchlorate must be between 70 - 130% of the MRL concentration. If the MRL recovery fails this criterion, the MCT should be lowered by 10% and this MRL verification must be repeated.

12.2.8.12. Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is above the MCT, sample dilution or pretreatment, as described in respective Sections 14.1.4. and 14.1.5. must be performed.

12.3. Assessing Laboratory Performance – The following items must be included in every analysis batch (Section 6.1.).

12.3.1. Laboratory Method Blank (MB): A MB must be prepared and treated exactly as a typical field sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with field samples. Data produced are used to assess instrument performance of a blank sample and evaluate contamination from the laboratory environment. Values that exceed ½ the MRL indicated a laboratory or reagent contamination is present. The source of the contamination must be determined prior to conducting any sample analysis. Any sample included in an automated analysis batch that has an invalid MB, indicated by a quantitated perchlorate that exceeds ½ the MRL must be reanalyzed in a subsequent analysis batch after the contamination problem is resolved.

12.3.1.1. When sample matrices have been pretreated to reduce the risk of high common anion interference, a second MB must be prepared, pretreated in exactly the same manner, and analyzed

to confirm no background effects from the pretreatment process are present. If an analysis batch only contains pretreated samples, then only a pretreated MB is required.

12.3.2. Instrument Performance Check (IPC) – The MCT, which was determined as part of the IDC in Section 12.2.8., must be verified through the analysis of an IPC. The IPC is three tiered and is used to verify the state of the IC system, over time, to quantitate perchlorate in highly ionic matrices. This must be conducted with each analysis batch since over time column performance can change.

12.3.2.1. Prepare a mixed common anion solution that reflects a conductance near (within ± 10%) that specified as the MCT. This solution must be prepared consistent with the instruction in Section 12.2.8., and containing the common anions chloride, sulfate and carbonate as well as perchlorate at a suggested concentration of 25 µg/L. This perchlorate concentration has been specified assuming the MRL has been set in the range of 3.0 µg/L to 5.0 µg/L. If a laboratory's MRL is higher, choose a perchlorate concentration for this exercise at approximately 5 times that of MRL.

12.3.2.2. Confirm the conductance of the IPC and analyze it as the initial sample in the analysis batch. If, after several weeks of storage, the measured conductance of this solution has shifted by more than 10% from the original measured value, prepare a fresh IPC solution. Following the analysis, calculate the $PD_{A/H}$ by comparing the peak area to height ratio of this IPC mixed anion standard (A/H_{MA}) for this analysis batch to the value that was derived for the LCS (A/H_{LCS}) either in the original IDC or in the previous analysis batch. As the first tier criteria, the value for the $PD_{A/H}$ must be less than 25% before proceeding with the analysis batch.

12.3.2.3. At the second tier criteria, the measured recovery for perchlorate in this IPC must fall between 80% and 120% (20.0 µg/L to 30.0 µg/L for a 25-µg/L fortification).

12.3.2.4. As a third tier and final criterion for the IPC, the laboratory must closely monitor the perchlorate retention time for this analysis. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if sudden shifts of more than 5% are observed in the perchlorate retention time, some type of instrument problem may be present. Potential problems included improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The observed retention time for perchlorate should closely replicate the times established when the column was originally installed. As a column ages, it is normal to see a gradual shift and shortening of retention times. If after several

years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column requires cleaning (according to manufacturer's instructions) or replacement. A laboratory should retain a historic record of retention times for perchlorate to provide evidence of an analytical column's continued performance.

12.3.2.5. If any conditions defined in Section 12.3.2.2. through 12.3.2.4. are not met, the MCT must be repeated and revised to a more appropriate lower matrix conductivity threshold or the source of the problem must be determined and the IPC reanalyzed.

12.3.3. Laboratory Control Sample (LCS): Prepare a secondary dilution stock using the same stock solution used to prepare the calibration standards. This separate, secondary dilution stock is used as a concentrate to fortify the LCS and the MS/MSDs. An external source stock or QCS, which is used to verify the accuracy of the calibration curve when it was initially prepared (Section 13.2.5.), should not be used to prepare this secondary dilution stock. Laboratories are required to analyze a LCS (filtered as if it were a field sample) with each analysis batch immediately following the ICCS. The LCS must be prepared with the same solution used to prepare the MS and should be prepared at concentrations no greater than ten times the highest concentration observed in any field sample, and may be varied as needed to reflect the range of concentrations observed in field samples. By analyzing the LCS initially, a control check is performed on the concentrated solution used to prepare the MS. If any deviations in the perchlorate concentration are present, it will be reflected in the LCS and not exclusively attributed to a matrix upon analysis of the MS. Calculate accuracy as percent recovery. The recovery for perchlorate must fall in the range of 85 - 115% prior to analyzing samples. If the LCS recovery for an analysis batch does not meet these recovery criteria, the data are considered invalid, and the source of the problem should be identified and resolved before continuing analyses.

12.3.3.1. When sample matrices have been pretreated to reduce the risk of high common anion interference, a second LCS must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects or recovery bias induced by the pretreatment are present. If an analysis batch only contains pretreated samples, then only a pretreated LCS is required.

12.4. ***Retention Time Window***

12.4.1. ***Prior to the analysis of samples, establish the retention time window for perchlorate.***

12.4.1.1. ***Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention***

time window width that does not accurately account for variations over several days.

12.4.1.1.1. ***Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte) or ± 0.1T_R (where T_R is the retention time of that analyte in the specified standard), whichever is greater.***

12.4.2. ***Daily retention time windows are based upon the retention time of the analyte in the CCV ± three times the mean standard deviation and are to be updated in the instrument method/data system after the analysis of the opening CCV (midpoint of the ICAL, if analyzed) and prior to further data processing.***

12.4.3. ***All subsequent standards in an analysis sequence must fall within the daily retention time window established by the first CCV. If not, identify the reason for the drift/shift, effect corrective action, and reanalyze any samples that are associated with/bracketed by those standards.***

12.4.4. ***If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.***

12.4.5. ***Occasionally, sample matrix may create a shift in the retention time window for a sample that may also impact the following CCV. In this case, reanalyze the sample to confirm that matrix effects are the reason for the shift and not the instrument. In addition, post spiking the sample to confirm that the peak is in fact perchlorate may be warranted in order to properly report the analyte in a sample.***

12.4.5.1. ***To post spike, estimate the concentration in the sample and then spike at a similar level. Reanalyze the post-spiked sample aliquot. If the peak is truly perchlorate, it should essentially double in height and area. If the peak appears to be split at a value greater than 20% resolution, and/or two peaks are clearly present, then it has not been confirmed. Additionally, LCMSMS (EPA 331 or 6850) may be used to confirm any questionable detections.***

12.4.6. ***Retention time windows shall be recalculated whenever a new column is installed.***

12.5. Assessing Analyte Recovery and Data Quality – The following must be included in every analysis batch (Section 6.1.).

12.5.1. Laboratory Matrix Spike (MS): The laboratory must add a known amount of each target analyte to a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. Samples which exceed the MCT, must either be diluted or pretreated to reduce the common anion levels. Samples that are pretreated have additional MS

requirements described in Section 14.1.5.6., and must be spiked before pretreatment. For a MS to be valid, the target analyte concentrations must be greater than the native level and should adhere to the requirement outlined in Section 12.4.1.2. It is recommended that the solutions used to spike the MS be prepared from the same stocks used to prepare the calibration standards and *not* from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

12.5.1.1. The spiked concentration must be equal to or greater than the native sample concentration. Spiked samples that exceed the calibration range must be diluted to be within the linear range. In the event that the spiked level is less than the observed native level of the unspiked matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the spiked concentration when the native sample concentration to spiked concentration ratio is greater than one.

12.5.1.2. For normal drinking waters, the MS typically should be prepared in the range of 20 - 50 µg/L, and for soils/solids in the range of 100 - 500 µg/kg. The MS should not be prepared at concentrations greater than ten times the highest concentration observed in any field sample and may be varied as needed to reflect the range of concentrations expected in field samples.

12.5.1.3. Calculate the percent recovery for each target analyte, corrected for concentrations measured in the unspiked sample. Percent recovery should be calculated using the following equation:

$$\%REC = \frac{(C_S - C)}{S} \times 100$$

where,

%REC = percent recovery.

C_S = measured perchlorate in the spiked sample.

C = measured native perchlorate sample concentration.

S = concentration equivalent of analyte added to sample.

12.5.1.4. Recoveries may exhibit matrix dependence. If the recovery for perchlorate falls outside 80 - 120%, and the laboratory's performance for all other QC performance criteria is acceptable, the accuracy problem encountered with the spiked sample is judged to be matrix related, not system related. The result for that analyte in the unspiked sample and the MS must be labeled suspect/matrix to inform the data user that the result is suspect due to matrix effects. Repeated failure to meet suggested recovery criteria indicates potential problems with the procedure and should be investigated.

12.5.2. Laboratory Duplicate or MS Duplicate – The laboratory must analyze either a laboratory duplicate or a MS duplicate for a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and ensure the quality of the data. Without prior knowledge or strong suspicion that an unknown sample has measurable perchlorate concentrations, the best alternative is to analyze an MS duplicate.

12.5.3. Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_C) and duplicate quantitated concentration (D_C) using the following formula.

$$RPD = \frac{|I_C - D_C|}{\frac{(I_C + D_C)}{2}} \times 100$$

12.5.3.1. Duplicate analysis may exhibit matrix dependence. If the RPD for the duplicate measurements of perchlorate falls outside ± 15% and if all other QC performance criteria are met, laboratory precision is out of control for the sample and perhaps the analytical batch. The result for the sample and duplicate should be labeled as suspect/matrix to inform the data user that the result is suspect due to a potential matrix effect, which led to poor precision. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses), it indicates a problem with the instrument or individual technique that must be corrected.

12.5.4. In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns (which meet the criteria in Section 9.1.2.2.), injection volumes, and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 12.2. and adhere to the condition of conductivity baseline stability found in Section 3.1.1.

12.5.5. It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant proficiency testing (PT) or performance evaluation (PE) sample studies.

13. CALIBRATION AND STANDARDIZATION

13.1. Demonstration and documentation of acceptable initial calibration is required prior to the IDC and before any samples are analyzed, and is required intermittently throughout sample analysis to meet required QC performance criteria. Initial calibration verification is performed using a QCS as well as with each analysis batch using an initial, continuing (when more than 10 field samples are analyzed), and end calibration check standards. The procedures for establishing the initial calibration curve are described in Section 13.2. The procedures to verify the calibration with each analysis batch are described in Section 13.3.

13.2. Initial Calibration Curve

13.2.1. Establish ion chromatographic operating parameters.

13.2.2. Estimate the Linear Calibration Range (LCR) – The LCR should cover the expected concentration range of the field samples and should not extend over more than two orders of magnitude in concentration. The restriction of two orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

13.2.2.1. If quantification is desired over a larger range, then two separate calibration curves should be prepared.

13.2.2.2. A minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude.

13.2.2.3. Since the anticipated concentration range for perchlorate in actual field sample is expected to cover two orders of magnitude, the use of at least five calibration standards in the range 4 - 400 µg/L is recommended. The initial calibration concentrations used are 2, 5, 10, 50, and 100 µg/L. An acceptable calibration has a correlation coefficient of 0.995 or greater.

13.2.3. Prepare the calibration standards by carefully adding measured volumes of the stock standard to a volumetric flask and diluting to volume with reagent water.

13.2.4. Inject 1250 µL of each calibration standard. Tabulate peak area responses against the perchlorate concentration. The results are used to prepare a calibration curve. Acceptable calibration is confirmed after reviewing the curve for linearity (second order fits are also acceptable) where r^2 is equal to 0.995 and passing the criteria for the initial calibration check standard in Section 13.3.1. Alternatively, if the ratio of area to concentration (response factor) is constant over the LCR (indicated by <15% relative standard deviation), linearity through the origin can be assumed and the average ratio or response factor can be used in place of a calibration curve.

13.2.4.1. Peak areas must be used as a measure of response since they have been found to be more consistent, in terms of quantitation,

than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites leading to peak broadening. Using peak areas, it is the analyst's responsibility to review all chromatograms to ensure accurate baseline integration of target analyte peaks, since poorly drawn baselines will significantly influence peak areas.

13.2.5. After establishing or reestablishing calibration curves, the accuracy of this calibration must be verified through the analysis of a QCS or an externally prepared second source. The QCS should be prepared at a concentration near the middle of the calibration curve. As specified in Section 12.2.5., determined concentrations must fall within ± 10% of the stated values.

13.3. Continuing Calibration Verification – Initial calibrations may be stable for extended periods of time. Once the calibration curve has been established it MUST be verified for each analysis batch, prior to conducting any field sample analysis using an Initial Calibration Check Standard. Continuing Calibration Check Standards and End Calibration Check Standards are also required as described in the sections below.

13.3.1. Initial Calibration Check Standard (ICCS) – For each analysis batch the calibration must initially be verified prior to analyzing any samples. The lowest level standard used to prepare the linear calibration curve must be used. In cases where the analyst has chosen to set the MRL above the lowest standard, a standard at a concentration equal to the MRL is acceptable. Percent recovery for the ICCS must be in the range of 75 - 125% before continuing the analysis batch and conducting any sample analyses.

13.3.2. Continuing Calibration Check/End Calibration Check Standards (CCCS/ECCS) – Continuing calibration check standards MUST be analyzed after every tenth field sample analysis and at the end of the analysis batch as an end calibration check standard. If more than 10 field samples are included in an analysis batch, the analyst must alternate between the middle and high continuing calibration check standard levels.

13.3.2.1. The percent recovery for perchlorate in the CCCS/ECCS must be within 85 - 115%.

13.3.2.2. If during the analysis batch, the measured concentration for perchlorate in the CCCS or ECCS differs by more than the calibration verification criteria shown above, or if the perchlorate peak retention time shifts outside the retention time window (as defined in Section 14.2.4.), all samples analyzed after the last acceptable check standard are considered invalid and must be reanalyzed. The source of the problem must be identified and resolved before reanalyzing the samples or continuing analyses.

13.3.2.3. In the case where the end calibration fails to meet performance criteria, but the initial and middle calibration checks are acceptable, the samples bracketed by the acceptable

calibrations may be reported. However, all field samples between the middle and end calibration checks MUST be reanalyzed.

13.4. Analytical Balance

13.4.1. Calibrate the analytical balance at 0.002 g (i.e., 2 mg), 1 g, and 100 g using Class 2 weights.

13.4.2. Calibration shall be within ± 10% at 0.002 g (± 0.0002 g), or within ± 0.1% at 1 g (± 0.001 g) and at 100 g (± 0.1 g). If the values are not within these limits, recalibrate the balance.

13.5. Top Loading Balance

13.5.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.5.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.6. Conductivity Meter Calibration – Prior to conducting the MCT and coinciding with each analysis batch, conductivity meter calibration must be verified or established using a standard KCl solution.

13.6.1. Thoroughly rinse the conductivity electrode with reagent water. Place the electrode in the reagent water, turn on the meter and confirm the conductance of this blank is <1 µS/cm.

13.6.2. Pour approximately 15 mL of the standard KCl solution into a plastic disposable micro beaker and place the electrode into the solution. The reference conductance for this solution is approximately 1000 to 1400 µS/cm at 25°C based upon the certified reference value using Fischer Scientific Traceable Conductivity Standards. Other values may be appropriate depending on the manufacturer of the KCl solution. The conductivity meter must yield a conductance reading of ± 5% of the referenced value to be in calibration.

13.6.3. If the conductivity meter fails calibration, recalibrate the unit per manufacture's instructions and repeat the procedure in Section 13.4.2. as if the standard solution were an unknown matrix.

14. PROCEDURE

14.1. Sample Preparation

14.1.1. Samples do not need to be refrigerated but if samples are held refrigerated as a standard practice for sample control, ensure the samples have come to room temperature prior to conducting sample analysis.

14.1.2. Soil and solid samples require extraction with de-ionized water prior to analysis, reference procedure in Appendix A.

14.1.3. Matrix Conductance Verification – Prior to conducting the analysis of a field sample matrix, the conductance of that matrix must be measured. Matrix

conductivity is directly related to the common anion levels that, at high concentrations, can influence the integrity of the perchlorate analysis.

14.1.3.1. Verify conductivity detector calibration by following the procedure outlined in Section 13.4.

14.1.3.2. Pour approximately 15 mL of sample into a plastic disposable micro beaker and reseal the sample bottle to protect the sample integrity.

14.1.3.3. Place the electrode into the matrix and measure the conductivity.

14.1.3.4. If the conductance is less than the MCT, continue to Section 14.1.6.

14.1.3.5. If the conductance is greater than the MCT, the matrix requires dilution or pretreatment prior to analysis. The dilution procedure is found in Section 14.1.4. Pretreatment is described in Section 14.1.5.

14.1.3.6. Discard this aliquot of sample and be certain to thoroughly rinse the electrode with reagent water between each matrix conductivity measurement.

14.1.4. Matrix Dilution – If matrix conductivity is less than the MCT, go to Section 14.1.6.

14.1.4.1. A sample can be analyzed once diluted with reagent water to a conductance below the MCT. The exact magnitude of this dilution will adversely increase the MRL by an equivalent proportion.

14.1.4.2. Knowing the matrix conductance exceeds the MCT, estimate the proportion required for the dilution by dividing the measured matrix conductance by the MCT. Round up to the next whole number and dilute the sample by a proportion equivalent to this value. For example, if the established MCT is 6100 µS/cm and a sample reflecting a conductance of 8000 µS/cm was measured, dilute the sample with reagent water by a factor of 2.

14.1.4.3. Measure the conductance of the diluted sample to confirm it is now below the MCT. Analyze the sample as specified in Section 14.1.6. with the understanding that the MRL has now been elevated by a proportion equivalent to the dilution.

14.1.4.4. If perchlorate is measured above the elevated MRL, determine the instrument sample concentration then multiply by the dilution factor to obtain actual field sample concentration and report. If no perchlorate is measured above the elevated MRL and analysis or project objectives required monitoring below the concentration of the elevated MRL, proceed to Section 14.1.5. and pretreat the matrix.

14.1.5. Pretreatment for Matrices Which Exceed the MCT – If matrix conductivity is less than the MCT, go to Section 14.1.6. If sample dilution did not yield the required results, sample pretreatment should be employed. When the MCT is exceeded, it is most often due to high levels of common anions (chloride, sulfate, and carbonate) in a particular matrix. If the analyst were to attempt the IC analysis of this particular matrix, the common anions present in the sample would distort the baseline and negatively affect the accurate quantitation of perchlorate. To effectively reduce a significant amount of the anions that contribute to the high conductivity reading, a series of pretreatment cartridges must be employed. For this pretreatment, three cartridges are attached in series in the following order: Ba, Ag, and H (for soil/solid matrix, RP, Ba, Ag, and H). It is recommended that all three (or four) cartridges be employed unless the analyst has specific knowledge that a matrix primarily has high levels of a specific common anion.

14.1.5.1. Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to ensure all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

14.1.5.2. Prior to pretreating any field samples, prepare and pretreat both an MB and an LCS. These pretreated quality control samples are required when an analysis batch contains a matrix that must be pretreated. This pretreatment is conducted by placing the cartridges in the following prescribed series (Ba → Ag → H; for soil/solid matrix, RP → Ba → Ag → H). The pretreated MB and LCS are used to verify that no background interference or bias is contributed by the pretreatment. If a response is observed in the pretreated LCS triple or quadruple the volume of reagent water rinse suggested by the manufacturer in Section 14.1.5.1. and repeat until a blank measures no more than ½ the MRL. If this additional rinsing procedure is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment.

14.1.5.3. Filter 3 mL of the sample through the series of rinsed, stacked cartridges as an initial sample rinse (Ba, Ag, and H; for soil/solid matrix, RP, Ba, Ag, and H) at a flow rate of one drop every 3 to 4 seconds (approximately 1.0 mL/min or less). This flow rate is critical to the pretreatment and must be carefully followed. Discard this fraction and begin collecting the pretreated sample aliquot of collected sample.

14.1.5.4. When sufficient volume has been collected, measure the conductance of the pretreated sample aliquot being certain the conductivity meter's probe has been thoroughly rinsed and excess water has been shaken from the tip. If the conductance is below the MCT, the sample is ready for analysis. If the conductance is still above the MCT, the flow rate through the pretreatment cartridge is likely too fast and the pretreatment

should be repeated with new cartridges. In some instances, double pretreatment cartridges may need to be applied. When this pretreatment is performed properly, U.S. EPA has found a 70% to 95% reduction in matrix conductance with good recoveries for perchlorate.

14.1.5.5. Place this aliquot of pretreated sample into an autosampler vial as described in Section 14.1.6.

14.1.5.6. In order to ensure data quality, all samples that fail the MCT and have been selected for pretreatment, as described in Section 14.1.5., must also be used to prepare an MS. This MS must be fortified with perchlorate at concentrations close to, but greater than, the level determined in the native sample prior to the pretreatment. Initially, the pretreated sample is analyzed and perchlorate level is determined. Then, a second aliquot of sample must be fortified with perchlorate, pretreated to reduce the high common anion levels, and analyzed to assess perchlorate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the pretreatment step appropriately. If the perchlorate recovery falls outside the acceptance range of 80 - 120% (Section 12.4.1.4.), that particular sample should be reported as suspect/matrix.

14.1.5.7. The pretreatments prescribed above are effective at reducing the chloride and sulfate content of a sample matrix but will not reduce matrix concentrations of other anions such as nitrate or phosphate.

14.1.6. Pour approximately 15 mL of sample into a micro beaker and reseal the sample bottle to protect the sample integrity. Using a Luerlock, plastic 10-mL syringe, withdraw approximately 10 mL of sample from the micro beaker and attach a 0.45-µm particulate filter which has been demonstrate to be free of ionic contaminants, directly to the syringe. Filter the sample into an autosampler vial or manually load the injection loop injecting a fixed amount of filtered, well-mixed sample. If using a manually loaded injection loop, then flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

14.1.6.1. If the autosampler vials or vial caps are designed to automatically filter the matrix as the sample is loaded on the IC system, this filtration procedure can be omitted and the sample can be directly transferred to the autosampler vial.

14.2. Sample Analysis

14.2.1. Follow the manufacturer's recommended operating conditions for the ion chromatograph. Included in the operating conditions is the estimated retention time for perchlorate, which has been achieved by this method.

Other columns, chromatographic conditions or detectors may be used if the requirements of Sections 3.1.1., 9.1.2.2. and 12.2. are met.

14.2.2. Establish a valid initial calibration and verify this calibration by conducting a QCS as described in Section 13.2.5. and complete the IDC. Initially, analyze the IPC solution, followed by the LRB. Then confirm the IC system calibration by analyzing an ICCS (Section 13.3.1.) and, if required, recalibrate as described in Section 13.2. Lastly, analyze the LCS.

14.2.3. Inject 1250 µL of each filtered sample. Use the same size loop for standards and samples. An automated constant volume injection system may also be used. Record the resulting peak size in area units and retention time for each analyte or utilize the data storage function of the instrument software.

14.2.4. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond ± 5% of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.

14.2.5. If the response of a sample exceeds the calibration range, the sample must be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration calibration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to approximately ± 25% the estimated concentration. The response generated by these three new high concentration calibration standards must not exceed the upper linear range for the conductivity detector. The latter procedure involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution and sample reanalysis, if required.

14.2.6. Should more complete resolution be needed between perchlorate and a coeluting, shoulder peak, the eluent may be diluted. This will spread out the peaks, causing later elution of perchlorate. Analysts are advised to carefully evaluate any of these eluent dilutions since when these eluent changes are incorporated, other coelutions may be encountered that are not initially evident. Additionally, the analyst must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria (Section 12.) and by reestablishing a valid initial calibration curve (Section 13.2.).

14.2.6.1. Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening, which will be more evident by shortened and broadened peaks. This will adversely affect the MDLs for each analyte.

14.3. Automated Analysis with Method 314.0

14.3.1. The laboratory may prepare large analysis batches that are run in an automated manner. When conducting automated analyses, careful attention must be paid to ensure sufficient volume of eluent in the reservoir is available to sustain extended operation. In order to ensure their data are of acceptable quality, ensure that all QC performance criteria are met throughout the analysis batch through subsequent careful inspection of the data.

14.3.2. Analysis sequences must be carefully constructed to meet required QC specifications and frequency. An acceptable sequence for a sample analysis batch, with all the method-required QC, is specified in Section 14.3.3.

14.3.3. Autosampler vials are loaded onto the sample tray and analytic processing commenced. The sample vials are loaded in the following order:

1) Instrument Blank (BLANK)
2) Quality Control Sample (QCS)
3) Instrument Performance Check (IPC)
4) Method Blank (MB)
5) Initial Calibration Check Standard (ICCS)
6) Laboratory Control Sample (LCS)
7) Laboratory Control Sample Duplicate (LCSD)
8) Samples (up to 10 if the batch containing more than 10 field samples)
9) Continuing Calibration Check Standard (CCCS)
10) Matrix Spike (MS)
11) Matrix Spike Duplicate (MSD)
12) Samples (remaining samples in the batch)
13) End Calibration Check Standard (ECCS)

14.3.4. Item 1 – An Instrument BLANK is used to verify the acceptability of instrument baseline. An acceptable BLANK (≤ MRL) is required prior to sample analysis. Reagent water is used for the Instrument BLANK.

14.3.5. Item 2 – A QCS is used to check the validity of the calibration curve with externally prepared test materials. The QCS must be obtained from a source different from that of the calibration standards. An acceptable QCS (±10% of stated value) is required prior to sample analysis.

14.3.6. Item 3 – An IPC contains fixed concentrations of perchlorate and mixed anions. It is used to evaluate the performance of the instrument system in three tiers. First, the $PD_{A/H}$ of conductance should be < 25%. Second, the %REC of perchlorate should fall between 80 to 120%. Third, the shift of the perchlorate retention time should be ≤ 5%. (See Section 12.3.2.)

14.3.7. Item 4 – The MB is a known matrix similar to the samples being analyzed, and is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used. An acceptable BLANK (≤ ½ MRL) is required prior to sample analysis. Reagent water is used for the Instrument BLANK.

14.3.8. For aqueous samples, the MB consists of dilution water.

14.3.8.1. One MB is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.3.9. Items 5 – An ICCS is used to verify the acceptance of the initial calibration on a continuing basis. An acceptable ICCS (75-125% of stated value) is required prior to sample analysis. The concentration of the standard must be at or below the MRL level.

14.3.10. Item 6 – A LCS is a known matrix that has been spiked with a known concentration of the target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control by measuring the percent recovery (%REC) of the spiked compound. (%REC calculation and acceptance criteria are in sections 12.4.1.3. and 12.3.3. respectively). The LCS is processed concurrently with the associated samples. In the processing of the LCS reagents and procedures identical to those for actual samples are used.

14.3.10.1. For aqueous samples, the LCS consists of the target analyte spiked into dilution water.

14.3.10.2. One LCS is required for every batch of 20 samples per matrix or portion thereof.

14.3.11. Item 7 – If needed due to limited volume or project requirements, the LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process expressed as relative percent difference (RPD). The RPD calculation and acceptance criteria are in Sections 12.4.3. and 12.4.3.1., respectively.

14.3.11.1. One LCSD is required for every batch of 20 samples per matrix or portion thereof.

14.3.12. Items 8 and 12 – Samples should be sufficiently diluted or subjected to cleanup procedures to ensure that the IC is not contaminated. In diluting or performing cleanups, it should be understood that increased reporting limits might result.

14.3.13. Item 9 – A CCCS is used to verify the previously established calibration curve, and to confirm accurate analyte quantitation for the previous 10 field samples analyzed. The concentration of the standard must be either at a middle or at the highest calibration level. The percent recovery must be within 85 – 115%.

14.3.14. Item 10 – The MS is the actual matrix spiked with a known concentration of the target analyte. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC) of the spiked compound (%REC calculation and acceptance criteria are in Sections 12.4.1.3. and 12.4.1.4., respectively).

The sample that is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.3.14.1. One MS is required for every batch of 20 samples per matrix or portion thereof.

14.3.15. Item 11 – The MSD is handled identically to the MS. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The precision is expressed as relative percent difference (RPD). The RPD calculation and acceptance criteria are in Sections 12.4.3. and 12.4.3.1., respectively).

14.3.16. Item 13 – An ECCS is used to verify the previously established calibration curve, and to confirm accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The concentration of the standard must be either at a middle or at the highest calibration level. The ECCS is not of the same concentration used for the CCCS. The percent recovery must be within 85 – 115%.

14.3.17. Set up the ion chromatograph in preparation for the analytical sequence.

14.3.18. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record the pertinent information in the run logbook.

14.3.19. Initiate the sequence.

15. CALCULATIONS

15.1. Identify perchlorate in the sample chromatogram by comparing the retention time of a suspect peak within the retention time window to the actual retention time of a known analyte peak in the calibration standard. If the perchlorate retention time has slightly shifted (generally toward shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.

15.1.1. If a low concentration of perchlorate is suspected in an unknown sample, but the retention time has drifted to the edge of the retention time window, a low level should be prepared from this sample matrix to confirm the matrix induced retention time shift. If the fortified sample reveals a split or shouldering peak response, the low concentration in the unfortified sample is likely an interferant and should not be reported as perchlorate.

15.2. Calculate sample concentrations using the initial calibration curve generated in Section 13.2.

15.3. Report ONLY those values that fall between the MRL and the highest calibration standards. Samples with a perchlorate response that exceeds the highest calibration standard concentration must be diluted and reanalyzed. When this is not possible,

the alternated calibration procedures describe in Section 14.2.5. must be followed. Samples with perchlorate identified but quantitated below the concentration established by the lowest calibration standard, may be reported with a "J" qualifier, (i.e., above the MDL but below the MRL) and therefore, not reported as a quantitated concentration.

15.4. Report results in µg/L for aqueous matrices or µg/kg for soil/solid matrices.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13. (Calibration and Standardization) shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

16.3.1. At the time of this writing, analyst performance data supports the ability to generate accurate and precise results. Current figures show an approximate accuracy of 99%, as compared to the assigned value in proficiency evaluation studies.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air-purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Data Interpretation

18.1.1. Establish the daily retention time window of the target analyte. The daily retention time window is the retention time of the analyte in the daily standard ± three times the standard deviation determined in the retention time window study.

18.1.1.1. Tentative identification of an analyte occurs when a peak from a sample or sample extract falls within the daily retention time window.

18.1.1.2. Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and effect appropriate corrective action.

18.1.2. Quantitation of the target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample or sample extract and the calibration standards.

18.1.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

18.1.2.2. Determine the concentration based on the initial calibration curve.

18.1.2.3. If the instrument response exceeds the calibration range, dilute the sample or sample extract and reanalyze.

18.2. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.3. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream. Instrument eluent may, after initial demonstration of levels ≤ 100 ppb, be disposed via the sanitary disposal inlet.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. "Determination of Perchlorate in Drinking Water Using Ion Chromatography." Revision 1.0, November 1999. Daniel P. Hautman and David J. Munch, US EPA, Office of Ground Water and Drinking Water; Andrew D. Eaton and Ali W. Haghani, Montgomery Watson Laboratories.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Soil and Solid Extraction Method.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Projects.

24. MODIFICATIONS

24.1. The following modifications to method EPA 314.0 are noted.

ECI SOP M709 Section	Reference Document EPA Method 314.0 Section	Summary of Modification
N/A	N/A	None.

25. REVISION HISTORY

Revision	Description	Author	Effective Date
2.4	Section 2: Update matrices. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample container and storage. Section 13: Update calibration. Section 23: Update appendices. Section 24: Add Modifications. Section 25: Add Revision History.	K. Burney	2013-02-18

Revision	Description (Cont.)	Author	Effective Date
3.0	Revise Sections 10 and 12. Update Sections 3 and 6 for consistency with the other SOPs.	L. Scharpenberg K. Chang	2015-10-02

Appendix A

SOIL / SOLID EXTRACTION METHOD

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 314.0, Perchlorate by Ion Chromatography – Additional Procedure for Soil / Solid Sample Extraction.

2. SCOPE AND APPLICATION

2.1. The procedure described herein either supersedes or is in addition to the standard procedure.

3. METHOD SUMMARY

3.1. Soil / solid samples are extracted by sonication with reagent water and prepared for analysis by ion chromatography.

4. EQUIPMENT AND SUPPLIES

4.1. Ultrasonic bath, VWR Scientific Aquasonic Model 550T or equivalent.

4.2. Centrifuge, 250−6000-rpm variable speed, 1−30-min digital timer, VWR International Clinical 200 Large Capacity Centrifuge or equivalent.

4.3. Specimen containers, 4.5-oz (120-mL), high density polyethylene (HDPE) or polypropylene, with polypropylene lids, disposable, or equivalent.

4.4. Centrifuge tubes, 50-mL, polypropylene, with polypropylene lids, disposable, or equivalent.

4.5. Graduated cylinders, 50-mL or other capacity, glass, Class A.

4.6. Syringe filtration apparatus:

4.6.1. Syringe, 10-mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

4.6.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing, disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

4.6.3. Filter, 0.20-µm effective pore size, 30-mm diameter, nylon membrane with 1-µm glass microfiber pre-filter, polypropylene housing, disposable, National Scientific Company F2502-2 Target Syringe Filter or equivalent.

4.6.4. Syringes and filters must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.

5. REAGENTS AND STANDARDS

5.1. Reagents

5.1.1. Reagent water, distilled or deionized.

5.1.2. Sand, washed, sea or standard Ottawa.

5.2. Standards

5.2.1. None.

6. PROCEDURE

6.1. Weigh 10 g of soil or solid sample into a 120-mL plastic specimen container.

6.2. Add 100 mL of de-ionized water.

6.3. Place in an Ultrasonic bath for approximately 30 minutes.

6.4. Decant 50 mL of aqueous leachate into a centrifuge tube.

6.5. Centrifuge for approximately 15 minutes.

6.6. Filter the leachate with 0.2-µm filter, if leachate appears relatively clean.

6.6.1. Highly turbid or colored leachates may require filtration with a 0.45-µm filter prior to the 0.2-µm filtration.

6.7. Method Blanks and Laboratory Control Samples must use washed sea sand, glass beads, or teflon chips as a substitute for the soil matrix.

6.8. Method Blanks, Matrix Spikes and Laboratory Control Samples must be filtered and processed in exactly the same manner as the associated samples.

6.9. After filtration the samples are ready for pretreatment procedure (if needed) using the same measurements and techniques as for aqueous samples noted in Section 14. of the main SOP.

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 314.0 Perchlorate by Ion Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.

4.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

4.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. No samples shall be analyzed without a valid LOD.

4.2. Limit of Quantitation (LOQ)

4.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.2.2. LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.

4.3. Event Based Quality Control (LCS and MBs)

4.3.1. Laboratory Control Sample (LCS)

4.3.1.1. The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."

4.3.1.1.1. Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

4.3.1.2. The LCS shall be analyzed at a minimum frequency of one per preparation batch.

4.3.1.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

4.3.1.3. The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.

4.3.2. Method Blanks (MBs)

4.3.2.1. The method blank is used to assess the preparation batch for possible contamination during the preparation and processing steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated.

4.3.2.1.1. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

4.3.2.2. The method blank shall be analyzed at a minimum of 1 per preparation batch.

4.3.2.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

4.3.2.3. The MB is considered to be contaminated if one of the following conditions is met.

4.3.2.3.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.3.2.3.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.3.2.3.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

4.3.2.4. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

4.3.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.4. Matrix Based Quality Control (MS/MSDs)

4.4.1. Matrix specific QC samples indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. The information from these controls is sample/matrix specific and would not normally be used to determine the validity of the entire batch.

4.4.2. The frequency of the analysis of matrix specific samples shall be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the test method.

4.4.2.1. Each preparation batch of samples must contain an associated MS and MSD using the same matrix collected for the specific DoD project.

4.4.2.1.1. If adequate sample material is not available, then the lack of MS/MSDs shall be noted in the case narrative.

4.4.2.2. Additional MS/MSDs may be required on a project-specific basis.

4.4.3. The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.

4.4.4. The results from MS/MSDs are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments.

4.4.5. Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.

4.4.5.1. For MS/MSD results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.

5. REFERENCES

5.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

Title: **STANDARD METHOD 5220D / EPA METHOD 410.4 / 410.4M, CHEMICAL OXYGEN DEMAND (COD) BY CLOSED REFLUX, COLORIMETRIC TECHNIQUE**

Document No. : SOP-M724
Revision No. : 2.2
Supersedes : 2.1

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PROPRIETARY INFORMATION STATEMENT

Revision 2.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 11/11/11
MANAGEMENT **DATE**

_____ 11-10-11
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. Standard Methods 5220D / EPA method 410.4 / 410.4M, Chemical Oxygen Demand (COD) by closed reflux, colorimetric technique

2. APPLICABLE MATRICES

2.1. This method covers the determination of COD in surface waters, ground waters, domestic/industrial wastewaters and soils, sediments and similar materials.

3. DETECTION LIMITS

3.1. The estimated quantitation limits EQLs for this method are 5 or 20 mg/L (low or high range) for aqueous samples and 50 to 200 mg/kg (low or high range), wet weight, for soil or solid waste. The EQLs will be proportionally higher for samples that require dilution.

4. SCOPE AND APPLICATION

4.1. The applicable range of the method is 5 to 900 mg/L for aqueous samples and 50 to 9000 mg/kg for soil or solid waste.

4.2. The Chemical Oxygen Demand (COD) test determines the quantity of oxygen required for oxidation of reduced species including organic matter in a water or solid sample using a specific oxidizing agent, temperature and time of reaction.

5. METHOD SUMMARY

5.1. Samples, blanks and standards in sealed tubes are heated in a COD reactor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the COD reactor, cooled, and measured spectrophotometrically at 600 nm.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed ***together*** with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts,

digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.5. Continuing Calibration Verification (CCV): Solution prepared with the same conditions used as the initial calibration solution. The CCV contains each target compound, including surrogates and internal standards where applicable. The CCV must be prepared from a source other than that used for preparing the initial calibration solution.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.13. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.14. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.15. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.16. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.17. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.18. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.19. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.20. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.21. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.22. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.23. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.24. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.25. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Chlorides are among the reduced species oxidized by dichromate and will cause erroneously high COD values if over 2000 mg/L Cl and not complexed. Therefore, sufficient mercuric sulfate is added to the reagents to complex chloride before the chloride reacts with the dichromate.

7.2. Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent, and; therefore, Silver sulfate is added as a catalyst to enhance the oxidation of volatile straight-chain aliphatic compounds.

7.3. Nitrite may cause a positive interference if present in appreciable amount. Sulfamic acid is added to eliminate this positive interference of nitrite.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, safety apparel and eyewear (i.e., lab coats and glasses) are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDS's) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Spectronic 20D spectrophotometer (Milton Roy Company) or equivalent.

9.2. HACH COD Reactor Model 16500-10 or equivalent.

10. ►REAGENTS AND STANDARDS

10.1. Stock potassium acid phthalate:

10.1.1. Dissolve 0.850 g in 800mL of distilled water and dilute to 1 liter.

10.1.1.1. The KHP must have been pre-dried at 120° C. 1 ml=1 mg COD.

10.2. Working Calibration Standards

10.2.1. Prepare COD working standard solutions for Low Range analysis of 5, 10, 20, 50, 100 and 150 ppm by diluting appropriate volumes of the stock standard ***with reagent water.***

10.2.2. Prepare COD working standard solutions for High Range analysis of 20, 50, 200, 400, 600 and 900 ppm by diluting appropriate volumes of the stock standard ***with reagent water.***

10.3. Premixed COD reagents in screw-cap vials containing 76% sulfuric acid, 0.20% potassium dichromate, 0.40% silver sulfate, 0.60% mercuric sulfate and 0.002% sulfamic acid.

10.4. Mercuric sulfate for chloride pretreatment.

10.5. Concentrated sulfuric acid for chloride pretreatment.

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Collect the samples in glass bottles if possible. Recommended sample container size is 250 ml for aqueous samples and 2 oz jars with teflon-lined caps for soil/solid samples.

11.1.1. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

11.2. Aqueous samples should be preserved with sulfuric acid to a pH < 2 and maintained ***at 0°C - 6°C*** until analysis.

11.3. Solid samples should be maintained ***at 0°C - 6°C until analysis.***

11.4. The holding time for aqueous samples preserved with sulfuric acid is 28 days and for solid samples is 14 days.

12. ►QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. All quality control data should be maintained and available for easy reference and inspection.

12.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 should be adhered, unless superseded in this document.

12.4. Method blank and sample duplicate are performed every twenty samples or a portion thereof.

12.5. SUMMARY OF QC CHECKS

12.5.1. Initial Calibration

12.5.1.1. A seven-point initial calibration, including an instrument blank, must be established and the linear curve of Absorbance AU versus Concentration must have an R^2 ***of ≥ 0.995.***

12.5.1.2. A new calibration curve must be prepared for each new lot of COD vials or when the daily CCV (as follows) is deemed unacceptable.

12.5.2. Continuing Calibration Verification (midpoint)

12.5.2.1. Following establishment of a valid initial calibration, a CCV (midpoint) standard must be analyzed following every 20 samples thereafter and at the end of the run sequence. If the percent difference (%D) is < 5%, the initial calibration is deemed valid and sample analysis may resume.

12.5.2.2. If this criterion is not met, the CCV is deemed unacceptable for sample analysis to resume. Reanalyze the CCV. If it remains unacceptable, effect corrective action and re-calibrate.

12.5.3. Event-based Quality Control (LCS/LCSDs and MBs)

12.5.3.1. One method blank is analyzed with every 20 samples, or portion thereof.

12.5.3.1.1. Ideally, the concentration of the MB should be less than the reporting limit (RL). If the concentration exceeds the RL, the source of contamination must be investigated and, if possible, eliminated. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and re-analyzed if the MB criterion is not met.

12.5.3.2. LCS/LCSD Pair (if no sample duplicate)

12.5.3.2.1. If there is insufficient sample to prepare a sample duplicate or if the RPD is not acceptable, a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) shall be analyzed for every 20 samples, or portion thereof.

12.5.3.2.2. If the LCS/LCSD is not acceptable, the problem must be identified, corrected and associated samples re-prepared and re-analyzed.

12.5.3.2.3. The acceptance criteria for LCS/LCSD are referenced in section 18.1.

12.5.4. Matrix-based Quality Control (Sample Duplicate) or (Matrix Spike/Matrix Spike Duplicate).

12.5.4.1. One sample duplicate is analyzed for every 20 samples, or portion thereof.

12.5.4.1.1. Under certain project programs a Matrix Spike (MS) / Matrix Spike Duplicate (MSD) are required. These are used in lieu of a batch Sample Duplicate.

12.5.4.2. If there is insufficient sample volume to perform a sample duplicate, a LCS/LCSD shall be performed.

12.5.4.3. The acceptance criteria for sample duplicates are as follows:

12.5.4.3.1. When the relative percent difference (RPD) of the sample duplicate is at or within the established

acceptance limits ***(0-25%)***, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method. The sample duplicate data shall be reported with the corresponding sample data.

12.5.4.3.2. If the RPD is not within the established acceptance limits, the analytical system performance shall be suspect.

12.5.4.3.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.5.4.4. The acceptance criteria for MS/MSDs are referenced in section 18.4

12.5.4.5. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Turn on spectrophotometer and allow to "warm-up" for 15 minutes. Set the wavelength at 600 nanometers (nm).

13.2. Prepare calibration standards as in section 10.

13.3. Preheat the COD reactor to 150°C.

13.4. Remove the cap ***from each of the low or high level*** COD ***vials and*** carefully add 2.5ml of the standard down the side of the vial such that if forms a layer on top of the reagents.

13.5. Carefully replace the cap and tighten moderately.

13.6. Thoroughly mix the contents of the sealed vial by shaking.

13.7. Repeat for each standard.

13.8. Place the vials in the COD reactor for 2 hours.

13.9. Turn off the COD reactor and allow vials to cool to room temperature.

13.10. Carefully wipe the outside surface of the vial clean with a Kimwipe or equivalent.

13.11. Insert each vial into the spectrophotometer and read and record the absorbance of each standard into the COD Excel spreadsheet calculator program, see example in Appendix 23.1.

13.12. Add the standard concentration and observed absorbance from each standard vial to the spreadsheet and note this into the COD logbook. Check that the R^2 value for the linear curve is ≥ 0.995. If not re-prepare the standards.

14. ▶PROCEDURE

14.1. Preheat the COD reactor to 150° C.

14.2. If sample has a chloride concentration > 2000 mg/L then follow the steps below. Otherwise, proceed to step 8.3.

14.2.1. Place 30 ml of the sample into an Erlenmeyer flask.

14.2.2. Add 10 mg mercuric sulfate for every mg of Cl present in the sample.

14.2.3. Carefully add 5 ml of concentrated sulfuric acid with stirring to the contents of the flask and mix thoroughly.

14.3. Remove the cap from a ***High Range (20 – 900 mg/L)*** COD vial. Carefully add 2.5 ml of aqueous sample or 0.25gm of solid sample down the side of the vial such that it forms a layer on top of the reagents. Carefully replace the cap and tighten moderately.

14.4. Thoroughly mix the contents of the sealed vial by shaking.

14.5. ***Process the standards, blanks, QC or duplicates exactly as the samples.***

14.6. Place the vials in the COD reactor for 2 hours.

14.7. Turn off COD reactor and allow vials to cool to room temperature.

14.8. Carefully wipe the outside surface of the vial clean with a Kimwipe or equivalent.

14.9. Read the observed absorbance and note into the COD logbook.

14.10. After all the samples are analyzed, input the absorbance for each sample into the COD Excel spreadsheet calculator program.

14.11. Record the calculated concentration from the spreadsheet for each sample into the COD logbook.

14.12. Print and retain the COD Excel spreadsheet and place into a sequentially arranged 3-ring notebook.

14.13. If any samples are noted below the High Range reporting level of 20 mg/L, re-analyze using Low Range vials that have a reporting level of 5 mg/L.

14.13.1. Remove the cap from a Low Range (5 – 150mg/L) COD Vial. Carefully add 2.5 ml of aqueous sample or 0.25gm of solid sample down the side of the vial such that it forms a layer on top of the reagents. Carefully replace the cap and tighten moderately.

14.13.2. Thoroughly mix the contents of the sealed vial by shaking.

14.13.3. Process the standards, blanks, QC or duplicates exactly as the samples.

14.13.4. Place the vials in the COD reactor for 2 hours.

14.13.5. Turn off COD reactor and allow vials to cool to room temperature.

14.13.6. Carefully wipe the outside surface of the vial clean with a Kimwipe or equivalent.

14.13.7. Read the observed absorbance and note into the COD logbook.

14.13.8. After all the samples are analyzed, input the absorbance for each sample into the COD Excel spreadsheet calculator program.

14.13.9. Record the calculated concentration from the spreadsheet for each sample into the COD logbook.

14.13.10. Print and retain the COD Excel spreadsheet and place into a sequentially arranged 3-ring notebook.

15. ▸CALCULATIONS

15.1. The percent difference (%D) is calculated as follows:

$$\%D = \frac{|C_P - C_M|}{C_P} \times 100$$

where: %D = percent difference
C_P = concentration as prepared
C_M = concentration as measured

Note: Concentrations must be in equivalent units

15.2. The relative percent difference (RPD) is calculated as follows:

$$\%RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: %RPD = relative percent difference
C_1 = original sample concentration
C_2 = duplicate sample concentration

Note: Concentrations must be in equivalent units

15.3. The % recovery of each LCS/LCSD compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The % recovery of each MS/MSD compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).

$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. Results shall be reported to two significant figures in mg/L for aqueous samples and mg/kg for solid samples.

15.6. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. ▸DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD ***are 80%-120% REC and 20% RPD.*** The LCS/LCSD must be within acceptance limits. If the LCS/LCSD is not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and the samples are not detected, the sample data can be reported without qualification.

18.3. The acceptance criteria for Sample Duplicate and MS/MSDs are as follows:

18.3.1. ***The sample duplicate RPD should be within 25% from its parent sample***.

18.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits ***of 70%-130% REC and 25% RPD,*** the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2.1. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.3.2.2. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of

the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.4. Additional information regarding internal quality control checks is provided in SOP-T020.

18.5. All concentrations shall be reported in µg/L(ppb) for water samples and µg/kg(ppb) for oil, soil and solid waste samples.

18.6. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ▸CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a reported compound, the group leader confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound. ***Or the data qualified and the issue narrated in the final report.***

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT ***detected*** in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

20.1.2. MS/MSD: Acceptability of the MS/MSD recoveries are subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCE

22.1. Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 5220D.

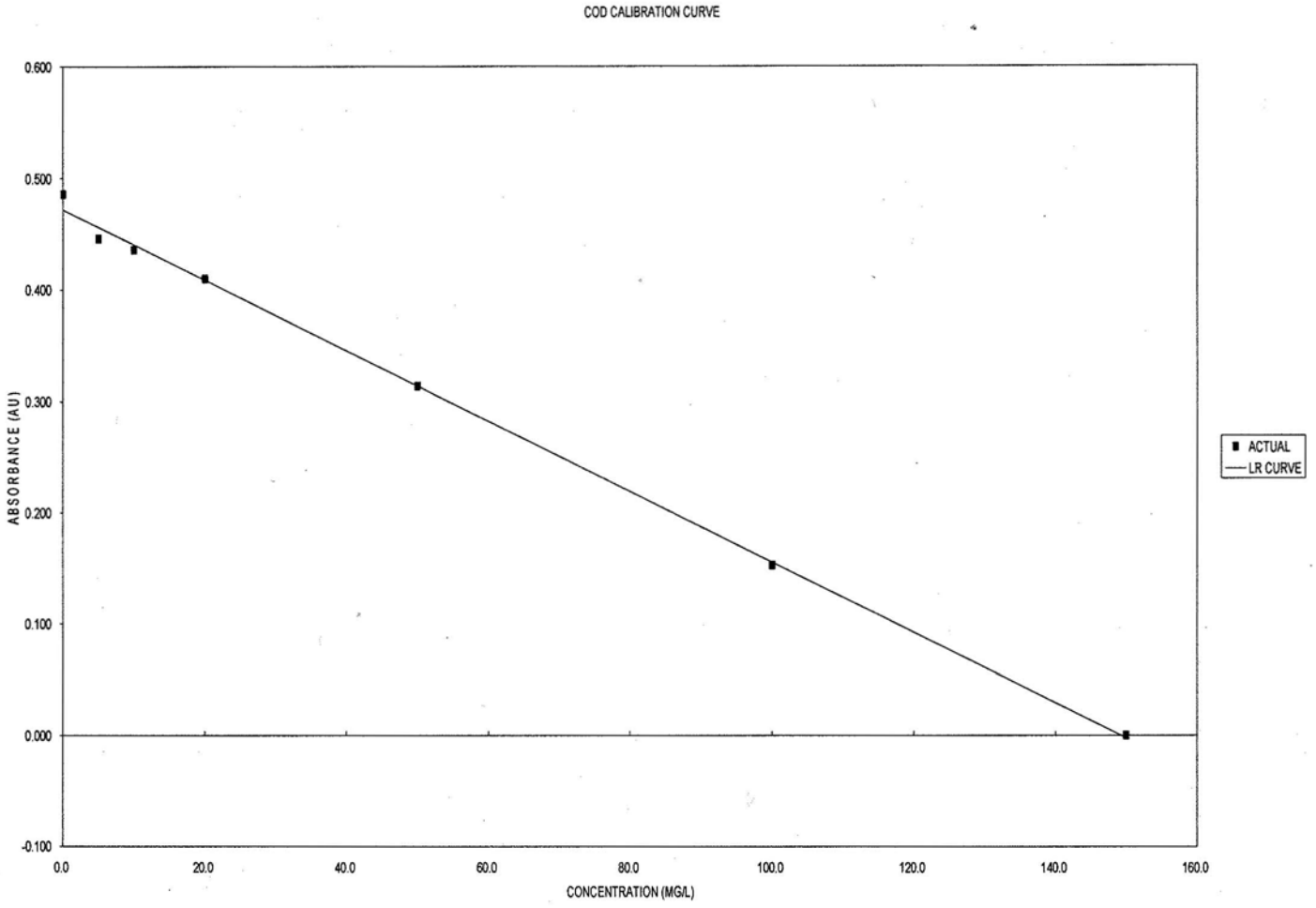
22.2. Methods for Chemical Analysis of Water and Wastes (MCAWW), EPA/600/4-79-020, Revised March 1983.

22.3. Bioscience, Inc., Twist-cap vial Method for Chemical Oxygen Demand (Spectrophotometric Method).

23. APPENDIX

23.1. *Appendix A:* Example Excel Spreadsheet Calculator

APPENDIX A: Example Excel Spreadsheet Calculator



Title : **EPA METHOD 504.1, 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) BY MICROEXTRACTION AND GAS CHROMATOGRAPHY**

Document No. : SOP-M412
Revision No. : 3.0
Supersedes : 2.0

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PROPRIETARY INFORMATION STATEMENT

Revision 3.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 10/15/14
MANAGEMENT **DATE**

_____ 10-15-14
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. EPA Method 504.1, 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) by Microextraction and Gas Chromatography.

2. APPLICABLE MATRICES

2.1. This method is applicable to finished drinking water and groundwater.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water
EDB	0.01 µg/L
DBCP	0.01 µg/L

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 504.1 is used to determine the concentrations of 1,2-dibromoethane or ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in water matrix. The method is used to quantitate EDB and DBCP without derivitization.

4.2. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 504.1 determination, either by regulatory reference or validation studies.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography (GC) and skilled in the interpretation of gas chromatograms.

5. METHOD SUMMARY

5.1. EPA Method 504.1 describes chromatographic procedures that will allow for the separation of EDB and DBCP in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. A 35mL aliquot of an aqueous sample is extracted with 2mL of hexane.

5.2.2. The extract is injected into a gas chromatograph equipped with a linearized electron capture detector for separation and detection.

5.2.3. Initial and continuing calibration standards and batch QC samples are prepared and processed in exactly the same manner as a field sample.

5.3. ***EPA Method 504.1 includes both the preparation and analytical procedure and should be referenced when reporting data. No other preparation procedure is applicable to this method. The preparation procedure for the standards and samples my be found in Section 14 of this SOP.***

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.5. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.6. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.7. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.8. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.9. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.10. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. ***Please refer to the current revision of the Eurofins-Calscience Quality Systems Manual for additional terms and definitions.***

7. ►INTERFERENCES

7.1. ***Dibromochloromethane (DBCM) is a common disinfection byproduct in chlorinated drinking waters that frequently occurs at relatively high concentrations. DBCM can elute very close to EDB, and a high concentration of DBCM may mask a low concentration of EDB, or be misidentified as EDB. Therefore, special care should be taken in the identification and confirmation of EDB.***

7.1.1. ***It is recommended that a DBCM standard is analyzed every time major maintenance is performed, including column changes or significant column trimming. A DBCM standard should be analyzed at least annually. It is recommended that it be analyzed quarterly.***

7.2. The dechlorinating agent, sodium thiosulfate, must be added to each sample to avoid the possibility of reactions that may occur between residual chlorine and indeterminant contaminants present in some solvents, yielding compounds that may subsequently interfere with the analysis.

7.2.1. The presence of sodium thiosulfate will arrest further formation of DBCM.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. The microextraction (liquid-liquid extraction) technique efficiently extracts a wide boiling range of non-polar organic compounds. It also extracts polar organic compounds with varying efficiencies.

7.5. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.5.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.5.2. Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition, suspected high level samples may be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.6. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, guard columns should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.7. ***Impurities contained in the extracting solvent usually account for the majority of the analytical problems.***

7.7.1. ***Solvent blanks should be analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the reagent water blanks. Whenever an interference is noted in the reagent water blank, the analyst should re-analyze the solvent.***

7.7.2. ***Interference-free solvent is defined as a solvent containing less than the MDL of an individual analyte interference. Protect interference-free solvents by storing in an area free of organochlorine solvents.***

7.8. ***It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.***

8. ►SAFETY

8.1. ***Extraction must be performed in a fume hood vented to the exterior of the laboratory.***

8.2. ***For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the extraction.***

8.3. ***To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform extractions alone. Another chemist should be present during any extraction process.***

8.4. EDB and DBCP have been tentatively classified as known or suspected human carcinogens. Primary standards of these compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.6. Material Safety Data Sheets (MSDSs) or Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS or SDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph or equivalent configured with splitless injection port, Agilent 7683B Series Autoinjector, or equivalent.

9.2. Instrument Software

9.2.1. Require a PC based data system or equivalent.

9.2.2. Agilent GC ChemStation Version 8.04.02[98] or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 30-m × 0.32-mm ID, 0.25-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused-silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.7.1. Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent. Use nitrogen as the alternative carrier gas if there is a helium supply shortage.

9.7.2. Any change in carrier gas(e.g. Nitrogen in place of helium) will prompt confirmation of MDLs, RLs and RT windows for the target analytes.

9.8. Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.9. Scintillation vials, 28-mm × 95-mm (40-mL capacity), screw top, clear glass, with Teflon- or aluminum foil-lined closed top screw caps and Teflon-lined septa, disposable.

9.9.1. Calibrate the scintillation vials by performing an equivalency study per each lot of the vials according to the procedure outlined in the current revision of SOP-T044. The volume and solvent used for the equivalency study are 35.0 mL of reagent water.

9.10. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp cap and Teflon-lined septa, disposable.

9.11. Vial inserts, 300−µL, clear glass, with conical bottom and spring.

9.12. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.13. Syringe, 5-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.14. Pipets, Pasteur, glass, disposable.

9.15. Weighing paper, 4-in × 4-in.

9.16. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.17. Equipment Software

9.17.1. None.

9.18. Equipment Maintenance and Troubleshooting

9.18.1. ***Routine maintenance shall be performed in order to optimize instrument performance. This includes, but is not limited to, replacing the injection port liner and trimming the column. Document all maintenance in the logbook.***

9.18.2. Refer to the user manual or equivalent document(s) of the specific equipment.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white granular powder, reagent grade or equivalent.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.3.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 200g of granular $Na_2S_2O_3$ in reagent water and dilute to 2 Liters with additional reagent water.

10.1.4. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.5. Methanol, CH_3OH, clear colorless liquid, HPLC grade or equivalent.

10.1.6. Sodium chloride, NaCl, anhydrous, white crystals, reagent grade or equivalent.

10.1.7. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, contain 200ppm of each target analyte, are used to prepare calibration and QC standards.

10.2.1.1. 200ppb Working Standards: Primary and Secondary:

10.2.1.1.1. Prepare the primary 200ppb working standard solution by diluting 50µL of the 200ppm stock standard to 50mL with methanol. ***Prepare in a 50ml volumetric flask.***

10.2.1.1.2. ***The second source standard shall be prepared in the same manner, at the same concentration, as the primary source.***

10.2.2. Calibration standard solutions contain various concentrations of target analytes in hexane.

10.2.2.1. ***Prepare each calibration standard solution according to the extraction procedure in Section 14.2.***

10.2.2.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)	Initial		Final Volume (mL)
	Concentration (ppb)	Volume (µL)	
0.15	200	1.5	2.0
2.50	200	25.0	2.0
5.00	200	50.0	2.0
10.00	200	100.0	2.0
20.00	200	200.0	2.0

Note: Final Volume = Hexane Extract Volume

10.2.2.3. The midpoint standard is also used as the continuing calibration verification (CCV) solution.

10.2.2.4. The calibration standards must be prepared fresh and extracted immediately after preparation on the day of calibration.

10.2.3. Initial calibration verification (ICV) solution contains 5.00ppb of each target analyte in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration.

10.2.3.1. Prepare the ICV solution according the procedure outlined ***in Section 14.2.***

10.2.3.2. The ICV solution must be prepared fresh and extracted immediately after preparation on the day of calibration.

10.2.4. Continuing calibration verification (CCV) solution contains 5.00ppb of each target analyte in hexane. The CCV solution is of a source same as that used for the initial five-point calibration.

10.2.4.1. Prepare the CCV solution according the procedure outlined ***in Section 14.2.***

10.2.4.2. The CCV solution must be prepared fresh and extracted immediately after preparation daily.

10.2.5. ***LCS and MS/MSD Spike Standards:***

10.2.5.1. 50ul of the 200ppb primary working standard is used for each QC sample. This equates to a spike level of 0.286ug/l.

10.2.6. All working standards must be replaced after one month or sooner if routine QC or comparison with check standards indicates a problem.

10.2.6.1. Store all working standards with minimal headspace and under dark and refrigerated conditions.

10.2.7. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.7.1. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40-mL pre-cleaned clear glass or amber glass VOA vials with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, add 0.5mL of 10% sodium thiosulfate solution per 40mL of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. If MS/MSD analyses are required, collect one sample in quadruplicate.

11.1.3. A reagent water trip blank, preserved in the same manner as the field samples, should accompany each batch of aqueous samples.

11.2. Samples shall be maintained in a chilled state (0−6°C), not frozen, post sample collection until received at the laboratory.

11.3. Upon receipt, the samples are stored in a 0−6°C cooler.

11.3.1. Aqueous samples must be solvent extracted within 14 days of sample collection.

11.3.2. All solvent extracts are then stored under dark and refrigerated (0−6°C) conditions and must be analyzed within 24 hours post solvent extraction.

12. ►QUALITY CONTROL

12.1. ***MDL verification sample***

12.1.1. ***An MDL verification sample, prepared at a level of 0.02ug/L, must be prepared and analyzed weekly.***

12.1.1.1. If this is an infrequent analysis (i.e., not performed weekly), the the MDL verification sample should be prepared and analyzed with every batch of samples.

12.1.1.2. If the low calibration standard is at or below this level (0.02ug/L) that may be used to demonstrate compliance with the MDL verification requirement.

12.2. Initial Calibration (IC)

12.2.1. The initial five-point calibration must be established prior to the processing of sample extracts.

12.2.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.3.1. If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.2.3.2. If the problem appears to be associated with a single calibration standard, then that one standard may be re-analyzed once within the same analytical shift prior to sample or QC analysis to rule out problems due to random chance.

12.2.3.2.1. In some cases, replacing the calibration standard may be necessary.

12.2.3.2.2. In all cases, a calibration point may not be dropped if it is from the middle of the curve. The first and/or last point may be dropped assuming that at least 5 points remain in the ICAL. If the low point is dropped, the RL must be elevated to that point.

12.2.3.3. If a calibration standard is replaced and/or re-analyzed, recalculate the RSD, and document the rationale for re-analysis on the run log and on the ICAL/Technical review form.

12.3. Initial Calibration Verification (ICV)

12.3.1. Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result on the run log and perform one of the following tasks.

12.3.3.1. Re-analyze the ICV once within 2 hours after the failed ICV.

12.3.3.2. Prepare a new ICV (includes the extraction process) and analyze once within 2 hours after the failed ICV.

12.3.3.2.1. In both of the above cases, the ICV may not be be analyzed if any other QC or sample extracts have been analyzed.

12.3.3.3. Evaluate the instrument conditions and re-process the calibration curve data.

12.3.3.4. If the ICV remains unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.3.4. If the initial calibration has been verified by the ICV, sample analysis may proceed.

12.4. Continuing Calibration Verification (CCV)

12.4.1. A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis.

12.4.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.2.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.3. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and perform the following tasks.

12.4.4.1. Re-analyze the CCV once within 2 hours after the failed CCV.

12.4.4.2. Document the reason(s) for re-analyzing the CCV and the corrective action(s) taken.

12.4.5. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.4.5.1. If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

12.4.5.2. If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

12.4.6. If the initial calibration has been verified by the CCV, sample analysis may proceed.

12.5. Retention Time Window

12.5.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.5.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte) or ± 0.030 minute, whichever is greater.

12.5.2. Establishment of retention time window position is accomplished by using the midpoint ICAL standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.5.2.1. When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.2.2. When initial calibration is not performed, daily retention time window for each analyte is the retention time of the analyte in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.3. Retention time for each analyte in the calibration verification standard is verified as follows:

12.5.3.1. When an ICAL is initially performed, the retention times for the ICV and all other CCVs within the 12 hour sequence must fall within the daily retention window established by the midpoint initial calibration standard.

12.5.3.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.5.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.6. Event Based Quality Control (MBs and LCS/LCSDs)

12.6.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS), and a laboratory control sample duplicate (LCSD).

12.6.2. Method Blank

12.6.2.1. The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

12.6.2.1.1. For aqueous samples, the MB consists of clean reagent water.

12.6.2.2. One MB is required every day that samples are prepared; for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.6.3. When samples that are prepared together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments.

12.6.3.1. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

12.6.4. The acceptance criteria for MBs are as follows:

12.6.4.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.6.4.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.6.4.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Refer to the current revision of SOP-T020 to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.6.5. Lab Control Sample (LCS):

12.6.5.1. The LCS is a known matrix which has been spiked with a known concentration of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

12.6.5.2. A LCS is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.6.5.3. The acceptance criteria for LCS compounds are as follows:

12.6.5.3.1. The lower and upper acceptance limits for %REC of each LCS compound are ***70% and 130%,*** respectively.

12.6.5.3.2. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, determine the cause of the problem and effect corrective action. Refer to the current revision of SOP-T020 to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.6.5.4. If the problem was not related to the extraction process, then the LCS and all associated QC sample extracts must be re-analyzed. If the failure was associated with the extraction process, then all associated samples must be re-extracted and re-analyzed in a new QC batch.

12.6.5.5. Prepare an LCS/LCSD when there is insufficient sample available to prepare an MS/MSD. ***The %RPD for the LCS/LCSD is $\leq$ 20%***

12.6.6. Matrix Spike / Matrix Spike Duplicate (MS/MSD)

12.6.6.1. The MS and MSD are made up of the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

12.6.6.2. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The MS in combination with the MSD can be used to assess the precision of the analytical measurements as well. The measurement is expressed as relative percent difference (RPD). The formulas for calculating %REC and %RPD are listed in Section 15, Calculations.

12.6.6.3. One MS/MSD pair is required for every batch of 20 samples per matrix or portion thereof extracted concurrently.

12.6.6.4. The acceptance criteria for MS/MSD compounds are as follows:

12.6.6.4.1. The lower and upper acceptance limits for %REC of each LCS compound are ***65% and 135%,*** respectively.

12.6.6.4.2. ***If an LCS/LCSD is ananlyzed, the RPD is ≤ 20%.***

12.6.6.4.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 75% and 115%, respectively. The RPD is ≤ 15%.

12.6.6.4.4. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.6.4.5. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in

these situations, refer to the LCS Specifically, an acceptable LCS usually supports matrix interference.

12.6.6.6. If the %REC or RPD of the LCS/LCSD and MS/MSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.7. Additional information regarding internal quality control checks is provided in the current revision of SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Calibration

13.1.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.1.1.1. Recalibration is required for the following maintenance procedures.

13.1.1.1.1. Change, replace, or reverse the analytical column.

13.1.2. After obtaining an acceptable five-point calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.1.3. The initial five-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.2. Retention Time Window Determination

13.2.1. Retention time window width for each analyte is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.2.2. Document the serial number of the analytical column associated with the retention time window study.

13.2.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

13.3. Top Loading Balance

13.3.1. Calibrate the top loading balance at 1g and 100g using Class 2 weights as outlined in the current revision of SOP-T043.

13.3.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

14. ▶PROCEDURE

14.1. Comparison Vial Preparation

14.1.1. ***A comparison vial is used to determine the volume of sample used in the preparation procedure. Water is withdrawn from the field vial using a Pasteur pipette, until the meniscus of the sample is even with the meniscus of the comparison vial; the 35ml mark..***

14.1.2. Tare a clean, calibrated scintillation vial on a calibrated top loading balance.

14.1.3. Measure 35.00g of clean reagent water into the vial, and label this vial as a comparison vial.

14.1.3.1. Assume the density of reagent water is 1mL/g at ambient temperature, therefore 35g = 35ml.

14.1.4. Cap and place the comparison vial on a flat surface.

14.1.5. Place all other vials next to the comparison vial to determine the proper volumn of sample.

14.2. Initial Calibration and Calibration Verification Standard Preparation

14.2.1. Allow a 200ppb working standard solution to reach ambient temperature.

14.2.2. Tare a clean, calibrated scintillation vial on a top loading balance.

14.2.3. Measure 35.00g of clean reagent water into the vial.

14.2.3.1. Assume the density of reagent water is 1mL/g at ambient temperature.

14.2.4. Add the appropriate volume of the 200ppb working standard solution to the reagent water using a syringe.

14.2.4.1. For the initial calibration (and CCV), spike the following volumes of the 200ppb Primary standard into the respective vials.

ICAL 1: 1.5ul of the 200ppb std (use a 10uL syringe)

ICAL 2: 25ul of the 200ppb std

ICAL 3/CCV: 50ul of the 200ppb std

ICAL 4: 100ul of the 200ppb std

ICAL 5: 200ul of the 200ppb std

14.2.4.2. For the initial calibration verification (ICV), add 50.0µL of the second source 200ppb working standard. (SA =5.0ppb in solution.)

14.2.4.3. For continuing calibration verification (CCV), add 50.0µL of the 200ppb primary working standard solution. (SA =5.0ppb in solution.)

14.2.4.4. Refer to section 10.2.7. for additional information on the ICAL standards. Use a syringe of appropriate volume for spiking:

14.2.5. Cap and label the vial appropriately.

14.2.6. Proceed to the sample preparation procedure.

14.3. Aqueous Sample Preparation

14.3.1. Allow an aqueous sample to reach ambient temperature.

14.3.2. Remove the cap and discard some volume of the aqueous sample using a Pasteur pipet.

14.3.3. Measure approximately 35mL of the aqueous sample by comparing the meniscus of the sample in the sample vial and the meniscus of water in the comparison vial. (Final volume will be determined by weight following extraction.)

14.3.3.1. For MB and LCS, measure 35mL of clean reagent water.

14.3.3.2. For MS/MSD, measure 35mL of the aqueous sample in each analytical batch selected for spiking.

14.3.4. Add 50.0µL of the ***200ppb primary*** working standard to each LCS and MS/MSD sample using a 50uL syringe.

14.3.5. Cap and label the vial appropriately.

14.3.6. Zero a top loading balance.

14.3.7. Weigh the sample vial on the top loading balance. Record the mass to the nearest 0.01g and record in the intial volume section of the preparation log.

14.4. Extraction

14.4.1. Remove the cap and add approximately 6g of anhydrous NaCl to the vial.

14.4.2. Cap and swirl the vial for approximately 20 seconds to dissolve the NaCl.

14.4.3. Remove the cap and add exactly 2.0mL of hexane to the mixture using a syringe.

14.4.4. Cap and shake the vial vigorously for 1 minute.

14.4.5. Allow the hexane layer to separate from the aqueous phase.

14.4.5.1. If the hexane extract will not be transferred to an autoinjector vial immediately, turn the vial upside down.

14.4.6. Remove the cap, carefully transfer the hexane extract (top layer) to a clean crimp-top autoinjector vial using a Pasteur pipet, and label the autoinjector vial appropriately.

14.4.6.1. Do not include any of the aqueous phase when transferring the hexane extract to the autoinjector vial.

14.4.6.2. If the analysis will not be performed immediately, store the hexane extract under dark and refrigerated (0−6°C) conditions.

14.4.7. Recap the vial and reserve until sample volume calculation.

14.5. Sample Volume Calculation

14.5.1.1. At the completion of the extraction step, calculate the volume of the aqueous sample extracted as follows:

14.5.1.2. Discard the contents that remain in the sample vial. Once empty, turn the vial upside down and shake briskly two or three times to remove any additional droplets in the vial.

14.5.1.3. Zero the same top loading balance as was used for the intial volume measurement.

14.5.1.4. Replace the vial cap.

14.5.1.5. Weigh the emptied sample vial on the top loading balance. Record the mass to the nearest 0.01g.

14.5.1.6. Calculate the volume of the aqueous sample used. Record the volume to the nearest 0.01mL. The formula for calculating volume is listed in Section 15.9.

14.5.1.6.1. Assume the density of an aqueous sample is 1mL/g at ambient temperature.

14.6. Documentation

14.6.1. Thoroughly document all aspects of the extraction in an extraction logbook. This logbook includes, but is not limited to:

14.6.1.1. Extraction date, start time, and end time.

14.6.1.2. Sample matrix, initial amount, and final volume.

14.6.1.3. Reagent identification number and amount.

14.6.1.4. Solvent identification number and volume.

14.6.1.5. Standard identification number, concentration, and volume added.

14.6.1.6. Analyst ID number

14.6.1.7. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.7. Analysis

14.7.1. Instrument Setup

14.7.2. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	splitless
Inlet temperature	220°C
Inlet pressure	7.89 psi
Purge flow rate	82.9 mL/min
Purge time	2.00 min
Total flow rate	89.0 mL/min
Carrier gas flow rate	1.7 mL/min
Makeup gas flow rate	30.0 mL/min
Detector temperature	300°C
Initial temperature	35°C, hold 2.00 min
Temperature program	35°C to 120°C at 12.00°C/min 120°C to 250°C at 35.00°C/min
Final temperature	250°C, hold 1.00 min

14.7.3. Autoinjector is set to inject 5µL of field or QC sample extract.

14.7.4. Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.

14.8. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.8.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.8.2. If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

14.8.3. If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV. ***This may entail reextracting the standards and samples.***

14.9. Following extraction, the extracts for the QC and actual environmental samples are received in autoinjector vials. he autoinjector vials are then loaded onto the GC sample tray.

14.10. Blank, standard, and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD) ***(If required)***
5) Method Blank (MB)
6) Samples (up to 20 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.10.1. The IB (or sovent blank) is a vial of hexane used to determine whether the GC system is free of interferants.

14.10.1.1. Additional instrument/soolvent blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples) to check for potential carryover or cross-contamination. The IB is optional.

14.10.2. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.11. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.12. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or sequence table printout.

14.13. Initiate the sequence.

14.14. Data Interpretation

14.14.1. Establish the daily retention time window for each analyte (Section 12.5).

14.14.1.1. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

14.14.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any analyte(s) in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.14.1.2.1. If any analyte(s) in the CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.14.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.14.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.14.2.2. Determine the concentration based on the initial calibration curve.

14.14.2.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the area of the characteristic peak. The formula for calculating concentration is listed in Section 15.7.

14.14.2.2.2. The data system is programmed to perform the calculation of concentration.

14.14.2.3. If the instrument response exceeds the calibration range, dilute the extract and re-analyze.

14.14.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.14.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.14.4.1. Report the result from the primary column.

14.14.4.1.1. Per client request or project specific data quality objectives (DQOs), report the higher result between the primary and confirmation column.

14.14.4.2. The %RPD between the results on the two columns must be ≤ 40%.

14.14.4.2.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak ***(such as DBCM)*** *is causing an erroneously high result (If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.*

14.14.4.2.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, then it may be appropriate to report the lower result.

14.14.4.2.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in

monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.14.4.3. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.14.4.4. A calibration curve and retention time window for each analyte are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.14.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.14.6. Confirmation is required for all positive results.

14.14.7. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023 and the data integrity policy.

14.14.7.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.14.7.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.14.7.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters in order to optimize the system..

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample ***solvent*** extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The volume of an aqueous sample used for solvent extraction is calculated as follows:

$$V_A = (M_1 - M_0) \times \rho$$

where: V_A = volume of aqueous sample used for solvent extraction in mL.
M_1 = mass of sample vial containing the aqueous sample in g.
M_0 = mass of sample vial in g.
ρ = density of aqueous sample in mL/g. Assume $\rho = 1$.

15.10. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor, sample or extract was diluted prior to analysis. If no dilution was made, D = 1.
V_f = volume of sample or extract after dilution in mL.
V_i = volume of sample or extract before dilution in mL.

15.11. All concentrations shall be reported in µg/L (ppb) for aqueous samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Refer to the current revision of SOP-T020 to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are ***70% and 130%, respectively. The RPD is ≤ 20%*** (between LCS and LCSD if analyzed). All LCS compounds must be within acceptance limits.

18.2.1. If the LCS %REC is outside of the acceptance limits high and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.3. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are ***65% and 135%, respectively. The RPD is ≤ 20%.***

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.1. for acceptance criteria.

18.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

18.5. Additional information regarding internal quality control checks is provided in the current revision of SOP-T020.

18.6. All concentrations shall be reported in µg/L (ppb).

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Director, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the Group Leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to re-analysis, depending upon the QC type in question.

20.1.1. LCS Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the Group Leader confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, refer to the current revision of SOP-T020 for procedures on data reporting and corrective action.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to re-analysis. No corrective action is required for that batch.

20.1.2. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic re-analysis of the batch samples. Rather, it is acceptable to defer to the LCS recoveries, to determine acceptance of the sample results.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Method 504.1: 1,2-Dibromoethane (EDB), 1,2-Dibromo-3-Chloropropane (DBCP), and 1,2,3-Trichloropropane (123TCP) in Water by Microextraction and Gas Chromatography*, Methods for the Determination of Organic Compounds in Drinking Water, Supplement III, EPA/600/R-95/131, USEPA, Revision 1.1, August 1995.

22.2. *1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) in Water by Microextraction and Gas Chromatography*, EPA Method 504.1, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Projects.

24. ►MODIFICATIONS

24.1. ***The following modifications from EPA Method 504.1 Revision 1.1 are noted.***

Calscience SOP M412 Section	Reference Document EPA 504.1 Section	Summary of Modification
10.2.4.	10.1.4	Varied, rotating CCV is not used.
11.1.1.	8.1.2	The amount of a dechlorinating agent added per 40mL aliquot of a sample is 50mg instead of 3 mg.
11.2.	8.2.1 and 8.3.1	Samples are maintained at 0−6°C instead of ≤ 4°C for transit and storage.
12.6.5.	9.1.4	One LCS per batch of 20 samples instead of one LCS (i.e., LFB) per batch of 10 samples are processed.
14.2	10.1.2	Calibration standard preparation procedure is modified. In particular, a top loading balance instead of a graduated cylinder or volumetric flask is used.
10.2.5.	9.3.1	LCS is spiked at approximately 0.286 µg/L instead of 0.25 µg/L in sample.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.3	Correct minor typos/grammar throughout. Section 6: Update definitions. Section 9: Update equipment. Section 11: Update sample container and storage. Section 13: Update calibration. Section 14: Update LCSD requirement. Section 23: Add appendix. Section 24: Add revision history.	J. Kang / L. Hunt	08/12/13
2.0	All: Revise the whole SOP to update existing procedures, reflect current laboratory practices, and conform to 2009 TNI Standard. Appendix A: Relocate extraction procedure from Section 14 to Appendix A. Appendix B: Update DoD requirements to DoD QSM Version 5.0.	Y. Patel / L. Hunt / K. Chang	04/17/14
3.0	All: Revise sections of the SOP to comply with the ELAP Audit findings: QC criteria, MDL verification sample. Elaborated on sample and QC preparation procedures. Removed Appendix A: Renamed Apendix B as Appendix A.	L. Scharpenberg	10/20/2014

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 504.1, 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) by Microextraction and Gas Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. Initial Calibration Verification (ICV)

4.1.1. The concentration of the ICV standard shall be at or near the midpoint of the calibration range.

4.2. Continuing Calibration Verification (CCV)

4.2.1. The concentration of the CCV standard shall be greater than the low calibration standard and less than or equal to the midpoint of the calibration range.

4.3. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. Detection limit (DL) determination shall be performed for each analyte at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following each DL determination and quarterly thereafter.

5.1.2.1. LOD verification sample shall be prepared by spiking a quality system matrix at a concentration of at least 2 times but no greater than 4 times the DL for each analyte.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio (S/N) of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations. This is initially estimated based on a minimum of 4 method blank analyses and later established with a minimum of 20 method blank results.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the DL determination and LOD verification.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.2.4. In situation where the test method is set up and used on an infrequent basis, LOD verification may be performed on a one per batch basis.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the calibration range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ for each analyte.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking a quality system matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.2.2.3. In situation where the test method is set up and used on an infrequent basis, LOQ verification may be performed on a one per batch basis.

5.3. Initial Calibration (IC)

5.3.1. The LOQ and the highest calibration standard establish the quantitation range.

5.3.1.1. When sample results exceed the quantitation range, dilute and re-analyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and re-analyze two consecutive CCVs within 1 hour after the failed CCV.

5.4.3.1. If these two CCVs pass, report both CCVs and the sample data without re-analysis.

5.4.3.2. If either of these two CCVs fails, or if the two CCVs cannot be analyzed within 1 hour, effective corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

5.5. Retention Time Window

5.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

5.5.1.1. When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S.

5.5.1.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte is the retention time of the analyte in the CCV standard ± 3S.

5.6. Event Based Quality Control MBs and LCS/LCSDs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the LOQ, <u>and</u> is greater than 1/10 the

amount measured in any associated sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds LOQ.

5.6.1.2. If the MB is contaminated, re-process the affected samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.6.1.2.1. If insufficient sample volume remains for re-processing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCS/LCSDs)

5.6.2.1. All reported analytes must be spiked. The concentration of each spike compound shall be at or below the midpoint of the calibration if project specific concentration is not specified.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, the laboratory's in-house control limits shall be applied.

5.6.2.2.1. The laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.

5.6.2.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (MS/MSDs)

5.7.1.1. All reported analytes must be spiked. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, the laboratory's in-house control limits shall be applied.

5.7.1.2.1. The laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

6.1.1. If CCV fails, refer to Section 5.4.3. of this appendix for corrective action.

6.2. Blank, standard, and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of the sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of extracts will result in increased reporting limits.

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 5.0, July 2013.

Title : **EPA METHOD 1625C(M), N-NITROSODIMETHYLAMINE (NDMA) BY ISOTOPE DILUTION GC/MS IN SELECTED ION MONITORING (SIM) MODE**

Document No. : SOP-M415
Revision No. : 2.0
Supersedes : 1.1

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PROPRIETARY INFORMATION STATEMENT

Revision 2.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 02/26/14
MANAGEMENT **DATE**

_____ 02-26-14
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. ►EPA Method ***1625C(M)***, N-Nitrosodimethylamine (NDMA) by Isotope Dilution GC/MS ***in Selected Ion Monitoring (SIM) Mode***.

2. APPLICABLE MATRICES

2.1. This method is applicable for water/aqueous matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are 2 ng/L for aqueous samples.

3.2. The ***RLs*** will be proportionally higher for samples that require dilution.

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedures on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. Until revised, this standard operating procedure is limited to the determination of n-nitrosodimethlyamine (NDMA).

4.2. This method is restricted to use by or under the supervision of analysts and supervisors who are experienced in the use of GC/MS and skilled in the interpretation of mass spectra.

5. ►METHOD SUMMARY

5.1. N-Nitrosodimethylamine detection is achieved using a Selected Ion Monitoring (SIM) mode for lower ***RL*** reporting for selected analytes.

5.2. N-Nitrosodimethylamine-d_6 is added to a 1-L wastewater sample. The aqueous sample is extracted at pH 12−13 using methylene chloride liquid-liquid technique. The final extract volume is 1 mL.

5.3. NDMA is separated and identified by the GC and MS, respectively. Identification involves the comparison of the sample analysis retention times and background-corrected spectral masses to the NDMA standard.

5.4. Quantitation is performed using the extracted ion current profile (EICP) areas. Isotope dilution is used, as this is readily available. Otherwise, the internal standard method may be employed.

5.5. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. The acceptable preparatory method is ***EPA Method 3520C, Continuous Liquid-Liquid Extraction. Refer to the current revision of SOP-M201***.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-

laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the injector or column. To minimize this effect, guard columns should be used and cut or replaced frequently. Also, the column can be "baked" after such samples.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. As a matter of routine, sample extracts with a dark color or high viscosity are subject to column Florisil cleanup prior to injection. In this procedure, a glass column is packed with Florisil and topped with a water adsorbent. Using methylene chloride as the solvent, separation of the target analytes and interferants is effected. Using the

solvent, the target analytes are eluted through the column while the Florisil retains the interferants.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats must be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDS)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph, Agilent 6890N Gas Chromatograph ***or equivalent*** configured with ***the following components:***

9.1.1. Autoinjector, Agilent 7683 ***Series or equivalent***.

9.2. Mass Spectrometer, Agilent ***5973Network*** Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the ***electron-impact ionization (EI)*** mode, ***and configured with the following components:***

9.2.1. ***Electron-ionization ion source.***

9.2.2. ***Hyperbolic quadrupole mass filter.***

9.2.3. ***High energy dynode (HED) electron multiplier (EM) detector.***

9.3. Instrument Software

9.3.1. Require a PC based data system or equivalent.

9.3.2. Agilent MSD ChemStation Version ***E.02.01.1177 or equivalent equipped with NIST mass spectral library***.

9.4. Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. ***Analytical*** Column: 30-m × 0.25-mm ID, 0.25-µm film thickness, ***non-polar, low bleed, narrow-bore, capillary, fused silica, J&W Scientific HP-5MS or equivalent***.

9.6. ***Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.***

9.7. ***Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.***

9.8. ***Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.***

9.9. ***Vial inserts, 300-µL, clear glass, with conical bottom and spring.***

9.10. ***Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.***

9.11. ***Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.***

10. ▶REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. ***Reagent water, interferant free.***

10.1.2. Methylene chloride ***(or dichloromethane), CH_2Cl_2, clear colorless liquid***, pesticide grade ***or equivalent***.

10.1.3. ***Refer to the specific SOPs of the preparatory methods for additional reagents.***

10.1.4. ***All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. Standards

10.2.1. Tuning standard solution containing 50 ppm of decafluorotriphenylphosphine (DFTPP) ***in methylene chloride***.

10.2.1.1. Inject 1.0 µL of the tuning standard for hardware tuning.

10.2.2. Pre-certified neat solutions of NDMA, sealed glass ampules and ***200*** ppb of surrogate are used to prepare 2-, ***100-, 200-, 400-, 800-ppb*** calibration standards on column, which are functionally equivalent to 2-, ***100-, 200-, 400-, 800-ppt in*** sample, taking into account the 1000:1 extraction concentration factor. NDMA-d_6 at ***800*** ppb is used as the internal standard. The ***200-ppb*** NDMA solution is also used as the ***continuing*** calibration verification ***(CCV) standard***.

10.2.3. Initial calibration verification (ICV) solution contains ***200-ppb*** of NDMA, the surrogate compound, and ***800*** ppb of the internal standard. The ICV solution must be of a source ***differing from*** that used for the initial five-point calibration. ***If it is of the same source, then it must be of different lot.***

10.2.4. Surrogate standard solution contains 1,4-dichlorobenzene-d_4.

10.2.5. The spike standard solution contains ***200-ppb*** NDMA.

10.2.5.1. ***This standard is used to prepare QC check samples such as laboratory control samples (LCS/LCSDs) and matrix spikes (MS/MSDs).***

10.2.5.2. ***Add 1.0 mL of the spike standard to each LCS/LCSD and MS/MSD sample prior to extraction. It is equivalent to 200 ppt in sample.***

10.2.6. ***All working standards must be replaced after six months (unless specified otherwise) or sooner if routine QC comparison with check standards indicates a problem.***

10.2.6.1. ***Store all working standards under dark and refrigerated condition.***

10.2.7. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2.7.1. ***Check all opened stock standards frequently for signs of degradation or evaporation.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures.

11.2. ***Aqueous*** samples ***shall*** be maintained in a chilled state ***(0−6°C), not frozen,*** post ***sample*** collection until received at the laboratory.

11.3. Upon receipt, the ***aqueous*** samples are stored in a ***0−6°C*** cooler.

11.3.1. Aqueous samples must be ***solvent*** extracted within 7 days of ***sample*** collection.

11.3.2. All ***solvent extracts*** are then stored under ***dark and*** refrigerated (***0−6°C***) conditions and must be analyzed within 40 days ***post solvent extraction***.

12. ►QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the tuning standard ***solution*** must be analyzed and meet the ***defined*** acceptance criteria.

12.1.2. ***The following criteria must be demonstrated every 12 hours.***

Mass	Ion Abundance Criteria
51	30 − 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 − 60% of mass 198
197	< 1% of mass 198

198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 – 23% of mass 442

12.1.3. ***If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action and re-tune the system.***

12.2. Initial Calibration ***(IC)***

12.2.1. The initial ***five-point*** calibration must be established prior to the processing of sample extracts.

12.2.2. ***The IC is deemed valid if*** the %RSD for ***each analyte is ≤*** 15%.

12.2.3. ***If*** the %RSD ***for an analyte*** is ≤ 15%, the relative response factor ***(RRF)*** is assumed to be constant over the calibration range, and the average ***RRF*** may be used for quantitation.

12.2.4. The relative retention time (RRT) ***of each analyte in each calibration standard*** should agree to within ± 0.06 RRT units.

12.2.5. If ***these criteria are*** not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.5.1. ***If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.***

12.2.5.2. ***If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.***

12.2.5.2.1. ***In some cases, replace the calibration standard may be necessary.***

12.2.5.3. ***If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.***

12.3. Initial Calibration Verification (ICV)

12.3.1. ***Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.***

12.3.2. The ***initial calibration*** is deemed valid if the %D for ***each analyte*** is ≤ 20%.

12.3.3. If ***these criteria are*** not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). ***Document the unacceptable result and perform one of the following tasks.***

12.3.3.1. ***Re-analyze the ICV once within 2 hours after the failed ICV.***

12.3.3.2. ***Acquire a new ICV standard solution and analyze once within 2 hours after the failed ICV.***

12.3.3.3. ***Evaluate the instrument conditions and re-process the calibration curve data.***

12.3.4. ***If the ICV remains unacceptable, investigate, effect corrective action, which may include replacement of standard solutions or instrument maintenance, and recalibrate.***

12.3.5. ***If the initial calibration has been verified by the ICV, sample analysis may proceed.***

12.4. ***Continuing Calibration Verification (CCV)***

12.4.1. Following the establishment of a valid initial calibration, a ***CCV*** standard must be analyzed ***daily prior to sample analysis and*** every 12 hours thereafter ***at the beginning of an analytical batch***.

12.4.2. The ***initial calibration*** is deemed valid if the %D for ***each analyte*** is ≤ 20%.

12.4.3. The internal standard response and retention time for the ***CCV*** must be evaluated ***during or*** immediately after data acquisition.

12.4.3.1. If the EICP area of any internal standard ***in a CCV standard*** changes by a factor of two ((−50% to +100%) ***from that*** in the midpoint ***calibration*** standard for the most recent initial calibration, the ***mass spectrometer*** must be inspected for malfunctions and corrective action effected.

12.4.3.2. If the retention time for any internal standard ***in a CCV standard*** changes by more than 30 seconds ***from that*** in the midpoint ***calibration*** standard for the most recent initial calibration, the ***gas chromatograph*** must be inspected for malfunctions and corrective action effected.

12.4.3.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.4. If ***these criteria are*** not met, the ***initial calibration*** is deemed unacceptable for sample analysis to resume. ***Document the unacceptable result and perform the following tasks.***

12.4.4.1. ***Re-analyze the CCV once within 2 hours after the failed CCV.***

12.4.4.2. ***Document the reason(s) for re-analyzing the CCV and the corrective action(s) taken.***

12.4.5. ***If the CCV remains unacceptable, effect corrective action and recalibrate.***

12.4.5.1. ***If a CCV fails, effect corrective action and recalibrate prior to analyzing any samples.***

12.4.6. ***If the initial calibration has been verified by the CCV, sample analysis may proceed.***

12.5. Event Based Quality Control (MBs and LCS/LCSDs)

12.5.1. ***Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS), and a laboratory control sample duplicate (LCSD).***

12.5.1.1. ***One LCS shall be prepared and processed to demonstrate the performance of the measurement system.***

12.5.1.2. ***One LCSD may be prepared and processed along with the LCS if one or more conditions as outlined in the current revision of SOP-T020 are met.***

12.5.2. ***The acceptance criteria for MBs are as follows:***

12.5.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. ***Refer to the current revision of SOP-T020*** to determine if the data should be qualified, or rejected and the samples ***re-processed*** and/or re-analyzed.

12.5.3. ***The acceptance criteria for LCS/LCSD compounds are as follows:***

12.5.3.1. ***The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.5.3.2. All LCS ***(including LCSD if required)*** compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, ***determine the cause of the problem and effect corrective action. Refer to the current revision of***

SOP-T020 to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.6. ***Matrix*** Based Quality Control (Surrogates, ***Internal Standards***, and MS/MSDs)

12.6.1. ***Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of surrogate(s) and internal standard(s) added to each sample, a matrix spike (MS), and a matrix spike duplicate.***

12.6.2. ***The acceptance criteria for surrogate compounds are as follows:***

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound ***are*** based upon the historical average recovery ± 3S ***that is updated at least annually***.

12.6.2.2. If the surrogate compound ***recoveries are*** acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If ***one or more surrogate recoveries are*** not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate ***recoveries do*** not invalidate sample data. The following must be accomplished if surrogate ***recoveries are*** not acceptable.

12.6.2.4.1. Check the ***surrogate and internal standard*** solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate ***recoveries***, the same ***sample*** should be ***re-processed or extract*** re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated ***standard*** solutions are determined to have not caused the unacceptable surrogate ***recoveries***, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate ***recoveries*** and the sample data reported with qualification.

12.6.2.4.3.1. If, upon ***re-processing*** and re-analysis, the ***surrogates remain***

unacceptable, matrix interference can be cited and reference made to the associated MB surrogate ***recoveries*** and the sample data reported with qualification.

12.6.2.4.3.2. If the MB ***surrogates are*** unacceptable, all associated sample data must invalidated and all associated samples ***re-processed*** and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery, which must be reported to the client.

12.6.3. ***The acceptance criteria for internal standard compounds are as follows:***

12.6.3.1. ***It is recommended that the internal standard responses (area counts) and retention times for each standard, sample, and blank be monitored for method performance, injection execution, system/instrument maintenance, analytical errors, or interferences.***

12.6.3.2. ***The area count of each internal standard peak in a standard, sample, or blank should be within 50% to 200% of that in the midpoint calibration standard for the most recent initial calibration.***

12.6.3.3. ***The retention time of each internal standard peak in a standard, sample, or blank should be within ± 30 seconds of that in the midpoint calibration standard for the most recent initial calibration.***

12.6.4. The acceptance criteria for MS/MSD ***compounds*** are as follows:

12.6.4.1. ***The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.***

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. ***Unacceptable %REC values are typically caused by*** matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. Additional information regarding internal quality control checks is provided in ***the current revision of*** SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. ***Mass Spectrometer Tuning***

13.1.1. Prior to ***initial calibration and*** the analysis of ***field or QC sample*** extracts, the GC/MS system must ***be hardware tuned such that the analysis of 50 ng or less of DFTPP meets the tuning criteria***. The acceptance criteria for the ***tune*** are listed in Section 12.1.

13.1.2. ***All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.***

13.1.3. ***Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.***

13.2. ***Mass Spectrometer Initial Calibration***

13.2.1. ***Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.***

13.2.1.1. ***Recalibration is required for the following maintenance procedures.***

13.2.1.1.1. ***Change, replace, or reverse the analytical column.***

13.2.1.1.2. ***Change the entrance lens, draw-out lens, or repeller.***

13.2.1.1.3. ***Change the electron multiplier and/or ion source chamber.***

13.2.1.1.4. ***Clean the ion source and/or quadrupole rods.***

13.2.2. After obtaining an acceptable five-point calibration curve and prior to processing ***field or QC sample extracts***, an ICV ***standard*** must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section ***12.3.***

13.2.3. The initial five-point calibration and ICV ***shall*** include ***all anticipated target analytes*** for the duration of the use of the initial calibration.

14. ►PROCEDURE

14.1. Following ***the*** establishment of a valid initial calibration, ***a CCV*** standard must be analyzed ***daily prior to sample analysis and*** every 12 hours thereafter ***at the beginning of an analytical batch. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume***. The acceptance criteria are listed in Section ***12.4.***

14.1.1. ***If a CCV fails, effect corrective action and recalibrate prior to analyzing any samples.***

14.2. Following extraction by the method specified in Section 5.5, the extracts of the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the ***system*** sample tray.

14.3. ***Standard and*** sample vials are loaded in the following or other ***logical*** order:

1) ***Tuning Standard***
2) ***Continuing*** Calibration Verification (***CCV***)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 ***per batch, excluding QC check samples and MBs***)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

14.3.1. ***Item 1: An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.***

14.3.2. Item ***2***: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable ***CCV*** is required ***daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch***.

14.3.3. Item ***3***: The LCS is a known matrix that has been spiked with a known concentration of the ***specific target analyte***. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.3.3.1. For aqueous samples, the LCS consists of the ***specified compound*** spiked into clean ***reagent*** water.

14.3.3.2. ***One*** LCS is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.3.4. Item ***4***: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section ***15.7.***

14.3.4.1. ***LCSD may be processed and analyzed if one or more conditions as outlined in the current revision of SOP-T020 are met.***

14.3.5. Item ***5***: The MB is a known matrix similar to the samples being analyzed that is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, internal standards, etc.).

14.3.5.1. For aqueous samples, the MB consists of ***clean reagent*** water.

14.3.5.2. ***One*** MB is required every day ***preparatory methods (i.e., extractions, cleanups, etc.)*** are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.3.5.3. When samples that are ***processed*** together are analyzed on separate instruments or ***on separate analytical shifts***, the MB associated with those samples must be analyzed on ***at least*** one of the instruments. A solvent blank ***consisting of methylene chloride must*** be analyzed on ***all*** other instruments ***where the associated samples are analyzed*** to demonstrate that the ***instruments are*** not ***contributing*** contaminants to the samples.

14.3.6. Item ***6***: Up to 20 sample ***(excluding QC check sample and method blank)*** extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.3.6.1. ***All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.***

14.3.7. Item ***7***: The MS is the actual matrix spiked with a known concentration of the ***specific target analyte***. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.3.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement

is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section ***15.6.***

14.3.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof ***processed*** concurrently.

14.3.8. Item ***8***: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section ***15.7.***

14.3.9. ***Solvent blanks consisting of methylene chloride may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration samples), to check for potential carryover or cross-contamination.***

14.4. Ensure that a sufficient amount of methylene chloride is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the ***instrument*** run logbook ***or on the sequence table printout***.

14.6. Initiate the sequence.

14.7. Data Interpretation

14.7.1. ***Evaluate the response (area count) and retention time of each internal standard compound in each standard, sample, and blank (see Section 12.6.3.).***

14.7.2. Qualitative identification of ***each analyte/surrogate*** is based on ***retention time of the sample component, and on*** comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

14.7.2.1. The reference mass spectrum ***must be generated using the same conditions of this method***.

14.7.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.7.2.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte.

14.7.2.3.1. When gas chromatographic peaks obviously represent more than one sample component ***(i.e., a broadened peak with shoulder(s) or a valley between two or more maxima)***, appropriate

selection of analyte spectra and background spectra is important.

14.7.3. ***Target analytes are identified as present when the following criteria are met.***

14.7.3.1. The intensities of the characteristic ions of ***an analyte*** maximize in the same scan or within one scan of each other.

14.7.3.1.1. Selection of a peak by a data system target ***analyte*** search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at an ***analyte-specific*** retention time will be accepted as meeting this criterion.

14.7.3.2. The ***relative retention time (RRT)*** of the sample target analyte is within ± 0.06 RRT units of the RRT of the standard analyte.

14.7.3.3. The relative intensities of the characteristic ions ***in the sample spectrum*** agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.7.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different ***GC*** retention times.

14.7.3.4.1. Sufficient ***GC*** resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.7.3.5. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of ***analytes***.

14.7.3.5.1. When ***analytes coelute***, the identification criteria ***may*** be met, but each ***analyte*** spectrum will contain extraneous ions contributed by the coeluting ***analyte***.

14.7.4. ***Tentative identification of a non-target analyte can be accomplished by using the data system library search. Refer to the current revision of SOP-T025 for procedure.***

14.7.4.1. ***The search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.***

14.7.4.2. ***The guidelines for making tentative identifications are as follows:***

14.7.4.2.1. ***Relative intensities of major ions (ions greater than 10% of the most abundant ion) in the***

reference spectrum should be present in the sample spectrum.

14.7.4.2.2. ***Relative intensities of major ions in the sample spectrum should agree within ± 20% of those in the reference spectrum.***

14.7.4.2.3. ***Molecular ions present in the reference spectrum should be present in the sample spectrum.***

14.7.4.2.4. ***Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting analytes.***

14.7.4.3. ***Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from sample spectrum due to background contamination or coeluting analytes. Data system library reduction program can sometimes create these discrepancies.***

14.7.5. Quantitation of a target analyte ***is*** based on the integrated abundance ***from the EICP*** of the primary characteristic ion.

14.7.5.1. ***Proper quantitation requires the appropriate selection of a baseline and integration from which the area of the characteristic ion peak can be determined.***

14.7.5.2. ***Determine the concentration based on the initial calibration curve.***

14.7.5.2.1. ***Calculate the concentration of each target analyte in a sample extract using the average of the initial RRFs, the area of the characteristic ion peak, and the internal standard concentration and ion peak area. The formula for calculating concentration is listed in Section 15.8.***

14.7.5.2.2. ***The data system is programmed to perform the calculation of concentration.***

14.7.5.3. ***If the instrument response exceeds the calibration range, dilute the sample and re-analyze.***

14.7.6. ***Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.***

14.7.6.1. ***When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.***

14.7.6.2. ***When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.***

14.7.6.3. ***Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.***

15. ▶CALCULATIONS

15.1. The response factor is calculated as follows:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: ***RRF = relative*** response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
C_{is} = concentration of internal standard ***in µg/L***.
A_{is} = area of the characteristic ion for internal standard.
C_x = concentration of target analyte being measured in ***µg/L***.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RRF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the ***RRFs*** for the target analyte.
RRF_{ave} = ***mean of the 5 initial RRFs*** for the target analyte.

15.3. The percent difference of each ***analyte*** is calculated as follows:

$$\%D = \frac{|RRF_{ave} - RRF_{daily}|}{RRF_{ave}} \times 100$$

where: %D = percent difference.
RRF_{daily} = ***daily RRF for the target analyte.***
RRF_{ave} = ***mean of the 5 initial RRFs for the target analyte.***

15.4. ***The relative retention time of each target analyte is calculated as follows:***

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.

RT_x = retention time of target analyte.
RT_{is} = retention time of internal standard.

Note: Retention times are in minutes to three decimal places.

15.5. The recovery of ***each*** LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The recovery of ***each*** MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.7. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.8. ***The target analyte concentration for a sample*** extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RRF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of internal standard in µg/L.

A_{is} = area of the characteristic ion for internal standard.
RRF_{ave} = ***mean of the 5 initial RRFs*** for ***the target analyte***.

15.9. ***The target analyte*** concentration for ***an*** aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in ng/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample ***solvent*** extracted in L.
D = ***dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.***

15.10. ***Refer to the preparatory method(s) for additional calculations.***

15.11. All concentrations shall be reported in ng/L (ppt) for ***aqueous*** samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. ***Refer to the current revision of SOP-T020*** to determine if the data should be qualified, or rejected and the samples ***re-processed*** and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S ***that is updated at least annually***. All LCS ***(including LCSD if required)*** compounds must be within acceptance limits ***(see Section 12.5.3. for additional information)***.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD ***(when applicable)*** is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.3. The acceptance criteria for surrogate compound recoveries vary depending upon historical data. The lower and upper acceptance limits for ***%REC of*** each surrogate compound ***are*** based upon the historical average recovery ± 3S ***that is updated at least annually***.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the surrogate and internal standard solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate ***recoveries***, the same sample ***should be re-processed*** or extract re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated ***standard*** solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be ***re-processed*** and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon ***re-processing*** and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed*** and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD ***compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each***

MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in ***the current revision of*** SOP-T020.

18.7. All concentrations shall be reported in ng/L (ppt) for aqueous samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. ►The Operations ***Director***, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ▶CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***Group Leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to re-analysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the ***Group Leader*** confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, ***refer to the current revision of SOP-T020 for procedures on data reporting and corrective action***.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to re-analysis. No corrective action is required for that batch.

20.1.2. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries

of an MS/MSD data set is does not constitute an automatic re-analysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. ▶REFERENCES

22.1. *Semivolatile Organic Compounds by Isotope Dilution GCMS*, Office of Science and Technology, Engineering and Analysis Division, Method 1625C, USEPA, June 1989.

22.2. *Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8270C, USEPA, Revision 3, December 1996.

23. ▶APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. None.

24. ▶MODIFICATIONS

24.1. The following modifications from EPA Method 1625C June 1989 Revision are noted.

Calscience SOP M415 Section	Reference Document EPA Method 1625C Section	Summary of Modification
1. and 5.	2.0	Procedures for solid sample preparation and analysis are excluded. Procedure for aqueous sample preparation is modified and referenced in SOP-M201. Target analyte quantitation is accomplished using GC/MS in SIM mode instead of full scan mode.
10.	6.0	Preparations of calibration and spike standard solutions are modified.
11.	9.0	Sample storage temperature is modified from 0−4°C to 0−6°C.
12.	5.12, 7.4, 8.0, and 12.0	Tune criteria are modified. Analytical shift is modified from 8 hours to 12 hours. Procedure and acceptance criteria for calibration with isotope dilution are modified. Control limits for ICV/CCV/LCS are modified.
14.	10.0	Procedures for sample preparation and extract cleanup are excluded.

25. ▶REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.1	Section 6: Add LOD/LOQ definitions. Section 9: Add software version and reference to SOP-T066 for instrument maintenance and troubleshooting. Section 24: Add modifications. Section 25: Add revision history.	Y. Patel	07/16/12
2.0	All: Revise the whole SOP to update existing procedures, add new quality control criteria, reflect current laboratory practices, and conform to 2009 TNI Standard.	Y. Patel / K. Chang	03/05/14

Title : **EPA METHOD 6010B, INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROMETRY (ICP-AES)**

Document No. : SOP-M601
Revision No. : 6.2
Supersedes : 6.1

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PROPRIETARY INFORMATION STATEMENT

Revision 6.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 5/2/2016
MANAGEMENT **DATE**

_____ 04-29-16
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 6010B, Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

2. APPLICABLE MATRICES

2.1. This method is applicable to groundwater samples, aqueous samples, mobility-procedure extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.2. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

3.2.1. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions.

3.2.2. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

4. SCOPE AND APPLICATION

4.1. EPA Method 6010B is used to determine trace elements, including metals, in solution. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require acid digestion prior to analysis.

4.1.1. Groundwater samples that have been prefiltered and acidified will not need acid digestion.

4.1.2. Samples which are not digested must either use an internal standard or be matrix matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards.

4.2. The method is applicable to the elements listed in Appendix A. Appendix A also lists the recommended analytical wavelengths and estimated instrument detection limits for the elements in clean aqueous matrices with insignificant background interferences. Elements and matrices other than those listed in Appendix A may be analyzed by this method if performance at the concentrations of interest (see Section 12.) is demonstrated.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of inductively coupled plasma emission spectrometer, skilled in the

interpretation of atomic emission spectra, and knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

5. METHOD SUMMARY

5.1. EPA Method 6010B describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

5.2. Background correction is required for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Section 7. should also be recognized and appropriate corrections made. Alternatively, multivariate calibration methods may be utilized. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

5.3. Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA/ICP	3005	SOP-M220
Acid Digestion of Aqueous Samples/Extracts for Total Metals for Analysis by FLAA/ICP	3010	SOP-M223
Acid Digestion of Sediments, Sludges, and Soils	3050	SOP-M222
Toxicity Characteristic Leaching Procedure (TCLP)	1311	SOP-M226
Synthetic Precipitation Leaching Procedure (SPLP)	1312	SOP-M227
Waste Extraction Test Procedure (STLC/TTLC)	CCR T22.11.5.A-II	SOP-M228

5.4. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

6. ►DEFINITIONS

6.1. Terms Specific to ICP-AES Analysis

6.1.1. Dissolved Metals: The concentration of metals determined in an aqueous sample after the sample is filtered through a 0.45-µm filter.

6.1.2. Instrument Detection Limit (IDL): A tool for evaluating the instrument noise level and response changes over time for analytes of interest. IDLs can be estimated by calculating the average of the standard deviations of three analytical runs performed on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples).

6.1.3. Interference Check Sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

6.1.4. Linear Dynamic Range: The concentration range above the highest calibration point over which the functional relationship between analyte signal and analyte concentration remains linear based on a one-point calibration. A sample result that falls within the linear dynamic range is considered valid and may be reported, thus avoiding the need to dilute and re-analyze the sample.

6.1.5. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The procedure is generally reserved for analyzing complex matrices. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.1.6. Optimum Concentration Range: A concentration range, below which scale expansion must be used, and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

6.1.7. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.1.8. Sensitivity: The average of the standard deviations of three runs of a reagent blank solution on three non-consecutive days with seven consecutive measurements per day.

6.1.9. Suspended Metals: The concentration of metals determined in the portion of an aqueous sample that is retained by a 0.45-µm filter.

6.1.10. Total Recoverable Metals (Total Acid Soluble Metals): The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid. "Total recoverable metals" is referred to herein as "total metals."

6.2. Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional definitions ***and glossaries.***

7. INTERFERENCES

7.1. Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

7.1.1. Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

7.1.2. To determine the appropriate location for off-line background correction, the analyst must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single-element solutions are sufficient. However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range.

7.1.3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Analysts may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Appendix B. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

7.1.4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al. According to Appendix B, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 0.01085 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.001085 mg/L. The analyst is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Appendix B. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

7.1.5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Analysts should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

7.1.6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced

interferences (see Appendix B) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst shall utilize a computer routine for automatic correction on all analyses.

7.1.7. Analysts using sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

7.1.8. If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank, the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

7.1.9. When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for 5 consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

7.1.10. When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

7.1.10.1. One method is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration, (i.e.,

less than the lower control limit of the calibration blank defined for a 99% confidence interval).

7.1.10.2. Another method is to analyze an interference check solution which contains similar concentrations of the major components of the samples (> 10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥ 20% of the analyte concentration, the analyte must be determined (1) using analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

7.2. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The dilution test (see Section 12.13.) will help determine if a physical interference is present.

7.3. Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

7.3.1. The MSA should be used if an interference is suspected or a new matrix is encountered. When the MSA is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences.

7.3.2. An alternative to using the MSA is to use the internal standard technique. Add one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium is often used. The concentration should be sufficient for optimum precision, but not so high as

to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

7.4. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to equal to or less than the method detection limit should be noted. Until the required rinse time is established, it is suggested that the rinse period be at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be re-analyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project specific data quality objectives (DQOs).

7.5. Analysts are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

7.6. The dashes in Appendix B indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

7.7. Clean chemistry methods and procedures are necessary in reducing the magnitude and variability of the calibration blank.

8. SAFETY

8.1. Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Hence, precautions must be taken to avoid inhalation, ingestion, or skin contact.

8.2. Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

8.3. All sample and standard preparation activities should be performed in an operational fume hood appropriate for use with acids.

8.3.1. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides.

8.3.2. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. ►Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the SDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Inductively Coupled Argon Plasma Emission Spectrometer, PerkinElmer Optical Emission Spectrometer Optima 5300 DV, PerkinElmer Optical Emission Spectrometer Optima 7300 DV, or equivalent configured with the following components:

9.1.1. Computer-controlled emission spectrometer with background correction.

9.1.2. Radio-frequency (RF) generator compliant with FCC regulations.

9.1.3. Mass-flow controller for argon nebulizer gas supply.

9.1.4. Peristaltic pump.

9.1.5. Autosampler, Perkin-Elmer AS 93plus Autosampler, PerkinElmer ESI SC-4 Autosampler, or equivalent.

9.2. Instrument Software

9.2.1. Require a PC based data system or equivalent.

9.2.2. ►PerkinElmer WinLab32 for ICP Version ***5.3.0.0656, PerkinElmer Syngistix for ICP Version 1.0.1.1275***, or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. ICP Torch and Nebulizer Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.5. Purge Gas: Nitrogen, N_2, 99.998%, cryogenic liquid, Praxair Nitrogen Cryogenic Liquid or equivalent.

9.6. Volumetric flasks, 100 mL, 500 mL, 1000 mL, or other capacity, glass, Class A.

9.7. Bottles, various sizes, PTFE fluoropolymers, polyethylene, or polypropylene, with screw caps.

9.7.1. Acid clean previously unused bottles with 1% HNO_3 solution prior to use.

9.8. Autosampler vessels, 16-mm OD (15 mL capacity), translucent polypropylene, disposal.

9.9. Autosampler vessels, 30-mm OD (50 mL capacity), with screw caps, translucent polypropylene, disposal.

9.10. Pipetters, 10–100 µL, 100–1000 µL, 0.5–5.0 mL, and 1–10 mL, calibrated, adjustable volume, with disposable tip.

9.11. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Chips, Teflon.

10.1.3. Beads, glass.

10.1.4. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, trace metals grade for equivalent.

10.1.5. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.5.1. Prepare the 1:1 HCl solution by slowly adding 500 mL of concentrated HCl to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.6. Nitric acid, HNO_3, 68.0–70.0% (v/v), concentrated, clear to yellow liquid, trace metals grade for equivalent.

10.1.7. Nitric acid, HNO_3, 1:1 (v/v).

10.1.7.1. Prepare the 1:1 HNO_3 solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.8. Rinse blank, HCl-HNO_3-H_2O, 1:1:8 (v/v/v).

10.1.8.1. Prepare the rinse blank by slowly adding 1 part of concentrated HCl and 1 part of concentrated HNO_3 to 8 parts of reagent water.

10.1.8.2. The rinse blank consists of 10% (v/v) HCl and 10% (v/v) HNO_3 in reagent water.

10.1.8.3. The rinse blank is used to flush the system between standards and samples to minimize memory interferences (see Section 7.4.).

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. ►Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions (ultra-high purity grade or equivalent), each in sealed polyethylene bottles, containing various concentrations of target analytes are used to prepare calibration and check standards.

10.2.1.2. Prior to preparing the calibration or check standards, analyze each stock standard solution separately to determine possible spectral interference or the presence of impurities.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for initial calibration.

10.2.2.1.1. If the addition of silver to the recommended acid combination initially results in a precipitate, then add the appropriate volume of reagent water and warm the flask until the solution clears. Cool and dilute to the appropriate final volume with reagent water. Higher concentrations of silver require additional HCl. Determine the stability the silver in the solution if necessary.

10.2.2.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the calibration standards ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.3. Blanks

10.2.3.1. Calibration Blank (CB)

10.2.3.1.1. Prepare the CBs by acidifying reagent water to the same concentrations of the acids found in the sample digestates prepared via EPA Method 3010.

10.2.3.1.2. The CB consists of 5% (v/v) HCl and 6% (v/v) HNO_3 in reagent water.

10.2.3.1.3. The CB is used to establish the zero point of the calibration curve.

10.2.3.1.4. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.3.2. Method Blank (MB)

10.2.3.2.1. Prepare the MBs using the appropriate sample preparation methods (see Section 5.3.).

10.2.3.2.2. The MB is used to identify possible contamination resulting from either the acids or the equipment used during sample processing including filtration.

10.2.3.3. Both CB and MB are required for the analyses of samples prepared by any method other than EPA Method 3040.

10.2.4. Initial Calibration Verification (ICV) Solutions

10.2.4.1. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for initial calibration.

10.2.4.1.1. Each target analyte in the ICV solution must be at a concentration within the established linear dynamic range.

10.2.4.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the ICV solutions ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.4.3. The ICV solution must be of a source differing from that used for the initial one-point calibration. If it is of the same source, then it must be of different lot.

10.2.5. Continuing Calibration Verification (CCV) Solutions

10.2.5.1. Dilute the appropriate volumes of the initial calibration standards with equal volume of calibration blank.

10.2.5.1.1. Each target analyte in the CCV solution is at a concentration near the midpoint of the calibration curve.

10.2.5.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the CCV solutions ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.5.3. Prepare the CCV solution fresh daily.

10.2.5.4. The CCV solution is of a source same as that used for the initial one-point calibration.

10.2.6. Internal Standard Solution

10.2.6.1. Prepare the internal standard solution by diluting the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to 2000 mL with reagent water.

10.2.6.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the internal standard solution ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.6.3. The internal standard solution contains 5 ppm each of Ho, Tb, and Y. It is used to reduce or overcome interferences (see Section 7.2. and Section 7.3.).

10.2.7. Potential Interference Check Solution

10.2.7.1. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the desired volumes with reagent water for potential interference check.

10.2.7.2. The potential interference check solution contains 200 ppm each of Al, Ca, Cr, Cu, Fe, Mg, Mn, Tl, and V. It is used to establish the potential interference table (see Section 12.1.).

10.2.8. Daily Spectral Interference Check Solutions (ICS-AB and ICS-A)

10.2.8.1. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for daily spectral interference check.

10.2.8.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the ICS-AB and ICS-A solutions ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.8.3. The ICS-AB and ICS-A solutions contain known concentrations of interfering elements. They are used to verify the interelement correction factors.

10.2.9. Spike Standard Solutions

10.2.9.1. Prepare the spike working standard solutions by diluting the appropriate volumes of the second source stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water.

10.2.9.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the spike working standard solutions ***if the commercially prepared custom reference standard solutions are unavailable***.

10.2.9.3. The spike standard solutions are used to prepare QC check samples such as laboratory control samples (LCS/LCSDs), matrix spikes (MS/MSDs), and post digestion spikes (PDSs).

10.2.9.4. The spike standard must be of a source differing from that used for the initial one-point calibration. If it is of the same source, then it must be of different lot.

10.2.9.5. Add 250 µL of the spike standard to each 50 mL aliquot of aqueous LCS/LCSD and MS/MSD sample prior to digestion.

10.2.9.6. Add 500 µL of the spike standard to each 2 g aliquot of solid LCS/LCSD and MS/MSD sample prior to digestion.

10.2.9.7. Add 50 µL of the spike standard to each 10 mL aliquot of PDS sample after digestion.

10.2.9.8. Add 250 µL of the spike standard to each 5 mL aliquot of mobility-procedure extract designated as LCS/LCSD and MS/MSD prior to dilution and acidification.

10.2.10. Linear Dynamic Range Solutions

10.2.10.1. Prepare a minimum of three different concentrations of the linear dynamic range solutions in the same acid matrix by diluting the spike standard solutions or the stock standard solutions. The analyst determines the applicable concentrations.

10.2.10.2. The linear dynamic range solutions contain various concentrations of compatible elements. They are used to establish linear dynamic range (see Section 12.6.).

10.2.11. All working standards must be replaced after the stock standard expiration dates (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.11.1. Add the appropriate types and volumes of acids such that the mixed standard solutions are matrix matched with the sample digestates.

10.2.11.1.1. If internal standards are utilized, then the types and volumes of acids added to a mixed standard solution do not need to be matrix matched with the sample digestates.

10.2.11.2. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together.

10.2.11.3. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage.

10.2.11.4. Demonstrate the stability of a low-level working standard (i.e., concentration < 1 ppm) prior to use.

10.2.12. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250 mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. Aqueous samples for dissolved metals determination shall be field filtered within 15 minutes of sample collection and preserved with 1:1 HNO_3 solution to pH < 2.

11.1.2. Aqueous samples for total metals determination shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2. Solid samples should be collected in 4 oz or 8 oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures, or 6 in decontaminated brass or stainless steel sleeves with Teflon-lined closures.

11.3. Mobility-procedure extracts should be collected in 3 oz pre-cleaned polypropylene digestion tubes with polypropylene lids, or 250 mL pre-cleaned HDPE containers with Teflon-lined closures.

11.3.1. Mobility-procedure extracts shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.3.2. If precipitate is observed upon the addition of 1:1 HNO_3 solution to a small aliquot of the mobility-procedure extract, do not acid preserve the mobility-procedure extract. Digest the mobility-procedure extract within 24 hours.

11.4. Aqueous and Solid samples shall be maintained in a chilled state (0–6°C), not frozen, post sample collection until received at the laboratory.

11.5. Upon receipt, the aqueous and solid samples are stored in a 0–6°C cooler.

11.5.1. Unfiltered aqueous samples for dissolved metals determination must be filtered as soon as possible, immediately preserved with 1:1 HNO_3 solution to pH < 2, and digested and/or analyzed within 6 months of sample collection.

11.5.2. Filtered aqueous samples with acid preservation (pH < 2) for dissolved metals determination must be digested and/or analyzed within 6 months of sample collection.

11.5.3. Filtered aqueous samples without acid preservation (pH ≥ 2) for dissolved metals determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion or analysis, and digested and/or analyzed within 6 months of sample collection.

11.5.4. Aqueous samples with acid preservation (pH < 2) for total metals determination must be digested and analyzed within 6 months of sample collection.

11.5.5. Aqueous samples without acid preservation (pH ≥ 2) for total metals determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 6 months of sample collection.

11.5.6. Solid samples must be digested and analyzed within 6 months of sample collection.

11.5.7. Mobility-procedure extracts with acid preservation (pH < 2) must be digested and analyzed within 180 days post mobility extraction.

11.5.7.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.5.8. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 180 days post mobility extraction.

11.5.8.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.6. Refer to the specific SOPs of the preparatory methods and Appendix D for additional information on sample collection, preservation, and holding time.

12. QUALITY CONTROL

12.1. Potential Interference Table

12.1.1. Following the initial instrument setup, the potential interference table (see Appendix B) must be established prior to initial calibration.

12.1.1.1. The potential interference table is established by analyzing the potential interference check solution (see Section 10.2.7.).

12.1.2. The potential interference table should be updated every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.2. Instrument Detection Limit (IDL)

12.2.1. The instrument detection limit for each analyte shall be performed at initial instrument setup.

12.2.1.1. The IDL in mg/L is determined by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a method blank with seven consecutive measurements per day.

12.2.2. The data and calculations should be kept on file.

12.3. Initial Calibration (IC)

12.3.1. The initial one-point calibration must be established daily prior to the processing of sample digestates.

12.3.1.1. The calibration curve is established with one calibration blank and one high-level calibration standard.

12.3.1.2. The concentration level of each analyte in the high-level calibration standard shall not exceed its anticipated linear dynamic range.

12.3.2. The IC is deemed valid if the replicate %RSD for each analyte is ≤ 5%.

12.3.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.4. Initial Calibration Verification (ICV)

12.4.1. Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.

12.4.2. The initial calibration is deemed valid if the replicate %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 10%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and re-analyze the ICV within 2 hours after the failed ICV. If the ICV remains unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.5. Initial Calibration Blank (ICB)

12.5.1. Immediately following the analysis of an ICV standard, an ICB must be analyzed prior to sample analysis.

12.5.2. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.5.3. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and re-analyze the ICB.

12.6. Linear Dynamic Range

12.6.1. Following the initial instrument setup, the upper limit of the linear dynamic range for each analyte must be established for each wavelength utilized prior to initial calibration.

12.6.1.1. The upper range limit is established for each wavelength by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range.

12.6.1.1.1. The concentration level of each analyte in the lowest concentration standard shall be at or below the RL.

12.6.1.2. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The

data, calculations and rationale for the choice of range made should be documented and kept on file.

12.6.2. Following the establishment of a valid initial calibration, the upper range limit must be checked every six months, and a new upper range limit should be determined whenever there is a significant change in instrument response.

12.6.2.1. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

12.6.3. The upper range limit is deemed valid if the %D for each analyte in a high-level check standard analyzed and quantitated against the calibration curve is ≤ 10%.

12.6.4. Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. Hence, non-linear second order curve may be used if the instrument allows it.

12.6.4.1. The effective range must be checked, and the correlation coefficient of the second order curve fit should be ≥ 0.995.

12.6.4.2. Non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

12.7. Daily Spectral Interference Check (ICS-AB and ICS-A)

12.7.1. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A solutions must be analyzed daily prior to sample analysis. Per client request or project specific DQOs, an ICS-AB solution must be analyzed at the end of sequence.

12.7.1.1. The daily spectral interference check solutions are utilized to verify either the accuracy of the interelement correction factors if interelement corrections are applied, or the absence of interferences if interelement corrections are not applied.

12.7.2. The ICS-AB is deemed acceptable if the %D for each analyte is ≤ 20%.

12.7.3. The ICS-A is deemed acceptable if the absolute value of the concentration for each non-spiked analyte is < RL (unless it is a verified trace impurity from one of the spiked analytes).

12.7.4. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and re-analyze the ICS-AB and/or ICS-A.

12.7.4.1. If an ICS-AB and/or ICS-A at the start of sequence are unacceptable, effect corrective action prior to analyzing any samples.

12.7.4.2. Per client request or project specific DQOs, if an ICS-AB at the end of sequence is unacceptable, effect corrective action and re-analyze all samples since the last acceptable ICS-AB.

12.7.5. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions, occurs.

12.8. Continuing Calibration Verification (CCV)

12.8.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence.

12.8.2. The initial calibration is deemed valid if the replicate %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 10%.

12.8.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and re-analyze the CCV within 2 hours after the failed CCV. If the CCV remains unacceptable, effect corrective action and recalibrate.

12.8.3.1. If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

12.8.3.2. If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

12.9. Continuing Calibration Blank (CCB)

12.9.1. Immediately following the analysis of a CCV standard, a CCB must be analyzed prior to sample analysis.

12.9.2. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.9.3. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and re-analyze the CCB.

12.9.3.1. If a failed CCB is the first of the day, effect corrective action prior to analyzing any samples.

12.9.3.2. If a failed CCB is not the first of the day, effect corrective action and re-analyze all samples since the last acceptable CCB.

12.10. Event Based Quality Control (MBs and LCS/LCSDs)

12.10.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS), and a laboratory control sample duplicate (LCSD).

12.10.1.1. LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.

12.10.2. The acceptance criteria for MBs are as follows:

12.10.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective limits specified in the project specific DQO. In the absence of project specific DQO, the concentrations of target analytes in an MB should be less than or equal to the respective RLs. If regulatory limits are available, the concentrations of target analytes in an MB should be less than 10% of the respective regulatory limits. If the concentration of any target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

12.10.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.10.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

12.10.3. The acceptance criteria for LCS/LCSD elements are as follows:

12.10.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20% (between LCS and LCSD).

12.10.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.10.3.2. All LCS (including LCSD if required) elements must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.10.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.10.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.10.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 - 90	4
51 - 70	3
31 - 50	2
11 - 30	1
< 11	0

12.10.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.10.3.7. If the problem was not related to the digestion process, then the LCS/LCSD and all associated sample digestates must be re-analyzed. If the failure was associated with the digestion process, then all associated samples must be re-processed and re-analyzed.

12.11. Matrix Based Quality Control (MS/MSDs)

12.11.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike (MS) and matrix spike duplicate (MSD).

12.11.2. The acceptance criteria for MS/MSD elements are as follows:

12.11.2.1. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20% (between MS and MSD).

12.11.2.1.1. If historical data is available, then the lower and upper acceptance limits for %REC and %RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.11.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.11.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.11.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.12. If the %REC or RPD of the LCS/LCSD and MS/MSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.13. Dilution Test

12.13.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrument detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.13.2. If this criterion is not met, a physical or chemical interference effect shall be suspect. Perform post digestion spike addition.

12.14. Post Digestion Spike (PDS) Addition

12.14.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10−100 times the RL.

12.14.2. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

12.14.3. If the %REC of the PDS element is not within the established acceptance limits, a matrix effect shall be suspect. Perform MSA (see Section 14.15.) on all samples in the same preparation batch per client request or project specific DQOs.

12.15. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Demonstration of Performance

13.1.1. Document the selection criteria for background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those

ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences.

13.1.2. Generate the data using the same instrument, operating conditions, and calibration routine to be used for sample analysis.

13.1.3. Keep the data on file and available for review.

13.2. Pipetter

13.2.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043.

13.3. Spectrometer Initial Calibration

13.3.1. Establish an acceptable one-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.3.

13.3.2. After obtaining an acceptable one-point calibration curve and prior to processing field or QC sample digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.4. and Section 12.5.

13.3.3. The initial one-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 30 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality.

14.1.1.2. Deviations from instructions provided by the instrument manufacturer must be documented and approved by the Group Leader.

14.1.1.3. Use the following ICP-AES operating conditions as guidance.

Description	Operating Condition
RF Power	1100~1450 watts
Viewing Height Axial Plasma Radial Plasma	 14~18 mm −1~5 mm
Argon Coolant Flow	15~19 L/min
Argon Nebulizer Flow	0.5~1.5 L/min

Description (Cont.)	Operating Condition
Sampler	
Pump rate	0.6~1.0 mL/min
Wash time	15 sec
Preflush Time	1 min
Read Time	2~10 sec
Read Delay Time	15 sec
Number of readings/replicate	2

14.1.1.4. Repeatable interference correction factors can be achieved by adjusting the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively.

14.1.2. Refer to Appendix A for specific wavelengths. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference.

14.1.3. Optimize the plasma operating conditions prior to the use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, but only is required when first setting up a new instrument, or following a change in operating conditions. Follow the instrument manufacturer's instructions to optimize the plasma operating conditions.

14.1.3.1. Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable (about 30 to 60 minutes of operation). While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

14.1.3.2. After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

14.1.3.3. Profile the instrument to align it optically as it will be used during analysis. Follow the instrument manufacturer's instructions for optimization in the axial and radial modes.

14.1.4. Align the torch viewing position weekly.

14.1.4.1. Aspirate a standard solution containing 10 mg/L of Mn for radial viewing and 1 mg/L of Mn for axial viewing.

14.1.4.2. Allow the instrument software to set the torch viewing position with the highest signal intensity.

14.1.4.3. For radial viewing, the intensity of Mn at 257.610 nm should be greater than 10000 counts. For axial viewing, the intensity of Mn at 257.610 nm should be greater than 700000 counts.

14.1.4.4. If these criteria are not met, effect corrective action and re-align the torch viewing position.

14.1.5. Check the sensitivity daily.

14.1.5.1. Aspirate a standard solution containing 7.5 mg/L of As and 7.5 mg/L of Pb.

14.1.5.2. For axial viewing, the standard emission count of As at 193.696 nm should be greater than 10000, and the standard emission count of Pb at 220.353 nm should be greater than 40000.

14.1.5.3. If these criteria are not met, perform instrument maintenance, re-align the torch viewing position, and check the sensitivity prior to initial calibration.

14.1.6. The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits (IDLs).

14.1.7. If either the instrument operating conditions (such as incident power or nebulizer gas flow rate) are changed, or a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

14.1.8. After completing the initial optimization of operating conditions, and before analyzing samples, an interelement spectral interference correction routine to be used for sample analysis must be established and initially verified.

14.1.8.1. A general description of spectral interferences and the analytical requirements for background correction are discussed in Section 7.

14.1.8.2. The criterion for determining the presence of an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls beyond ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit.

14.1.8.3. Once established, the entire routine must be verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verifications of the routine should be kept on file.

14.1.9. Before daily calibration, and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

14.1.10. For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

14.1.11. Program the system to average a minimum of two integrations (i.e., replicate readings) on each blank, standard, and sample. Report the average.

14.1.11.1. If the %RSD for an analyte in a standard is > 5%, re-analyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.11.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, re-analyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

14.2.1. Establish method detection limits (MDLs) for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. Additional information regarding determination of detection limits is provided in SOP-T006.

14.2.2. Establish the upper limit of the linear dynamic range for each wavelength utilized (see Section 12.6.).

14.2.3. Verify that the instrument configuration and operating conditions satisfy the analytical requirements, and maintain quality control data confirming instrument performance and analytical results.

14.3. Establish a calibration curve to cover the appropriate concentration range (see Section 13.3.).

14.4. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A solutions must be analyzed daily prior to sample analysis. Per client request or project specific DQOs, an ICS-AB solution must be analyzed at the end of sequence. The acceptance criteria are listed in Section 12.7.

14.4.1. If an ICS-AB and/or ICS-A at the start of sequence are unacceptable, effect corrective action prior to analyzing any samples.

14.4.2. Per client request or project specific DQOs, if an ICS-AB at the end of sequence is unacceptable, effect corrective action and re-analyze all samples since the last acceptable ICS-AB.

14.5. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.8. and Section 12.9.

14.5.1. If a failed CCV/CCB is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

14.5.2. If a failed CCV/CCB is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV/CCB.

14.6. Following digestion by one of the methods specified in Section 5.3., the digestates for the QC and actual environmental samples are received in digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels are then loaded onto the ICP-AES sample tray.

14.6.1. Preliminary treatment of most matrices is necessary due to the complexity and variability of sample matrices.

14.6.2. Acid digestion is not necessary if groundwater samples for dissolved metals determination are prefiltered and acidified prior to analysis.

14.6.2.1. All associated QC samples (i.e., MB, LCS/LCSD, MS/MSD, and PDS) in the same preparation batch must undergo the same filtration and acidification procedures.

14.6.2.2. Samples which are not digested must either use an internal standard or be matrix-matched with the standards.

14.7. Blank, standard, and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Interference Check Solution AB (ICS-AB)
6) Interference Check Solution A (ICS-A)
7) Continuing Calibration Verification (CCV)
8) Continuing Calibration Blank (CCB)
9) Method Blank (MB)
10) Laboratory Control Samples (LCS)
11) Laboratory Control Sample Duplicates (LCSD)
12) Samples (up to 10 per batch, including QC check samples and MBs)
13) Matrix Spike (MS)

14) Matrix Spike Duplicate (MSD)
15) Dilution Test Sample (per client request or project specific DQOs)
16) Post Digestion Spike (PDS) (per client request or project specific DQOs)
17) Ending ICS-AB (per client request or project specific DQOs)
18) Ending CCV
19) Ending CCB

14.7.1. Item 1: The CB is an aliquot of acidified reagent water used to establish the zero point of the initial calibration curve.

14.7.2. Item 2: The initial calibration standard is a high-level calibration standard used to establish the initial calibration curve.

14.7.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial one-point calibration. An acceptable ICV is required immediately following initial calibration.

14.7.4. Item 4: The ICB is an aliquot of acidified reagent water used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.7.5. Items 5, 6, and 17: The ICS-AB and ICS-A are used to verify the accuracy of the interelement correction factors. An acceptable ICS-AB and ICS-A are required daily prior to sample analysis. Per client request or project specific DQOs, an acceptable ICS-AB is required at the end of sequence.

14.7.6. Items 7 and 18: A CCV is a standard used to verify the acceptance of the initial one-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence.

14.7.7. Items 8 and 19: A CCB is an aliquot of acidified reagent water used to monitor contamination. An acceptable CCB is required immediately following CCV.

14.7.8. Item 9: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.7.8.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of clean Teflon chips (or glass beads). For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.7.8.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.8.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one

of the instruments. A solvent blank consisting of acidified reagent water must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.7.9. Item 10: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.7.9.1. For aqueous samples, the LCS consists of the specified elements spiked into clean reagent water. For solid samples, the LCS consists of the specified elements spiked into clean Teflon chips (or glass beads). For mobility-procedure extracts, the LCS consists of the specified elements spiked into the mobility-procedure extract designated as LCS.

14.7.9.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.10. Item 11: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.7.10.1. LCSD is processed and analyzed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific data quality objectives (DQOs).

14.7.11. Item 12: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.7.11.1. All dilutions should keep the responses in the upper half of the linear range of the curve.

14.7.11.2. Digestates with concentrations exceeding the calibration range but within the linear dynamic range may be reported without dilution per client request or project specific DQOs.

14.7.12. Item 13: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the

processing of the MS, reagents and procedures identical to those for actual samples are used.

14.7.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.7.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.7.13. Item 14: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.7.14. Item 15: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.7.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.7.14.2. To comply with client request or project specific DQOs, one dilution test sample is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.7.15. Item 16: The PDS is the same sample matrix from which the MS/MSD samples were prepared or from another sample in the same preparation batch, and is spiked with known concentrations of specific target analytes post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.7.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.7.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.7.16. Rinse blanks or solvent blanks consisting of acidified reagent water may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample digestates), to rinse the analytical system or check for potential carryover or cross-contamination.

14.7.16.1. The rinse time is set to one minute. Rinse time may be reduced through a suitable demonstration.

14.8. Ensure that a sufficient amount of internal standard solution is present in the standard vessel at the beginning of the sequence.

14.9. Ensure that a sufficient amount of rinse blank is present in the rinse blank bottle, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.10. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.10.1. Record the reagent and standard identification numbers on the sequence table printout.

14.11. Initiate the sequence.

14.12. Dilution test and post digestion spike addition (see Section 12.13. and Section 12.14.) are recommended prior to reporting concentration data for the elements.

14.12.1. It is recommended that these tests be performed with each batch of samples prepared/analyzed to ensure that neither positive nor negative interferences are affecting the measurement of any element or distorting the accuracy of the reported values.

14.13. If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

14.14. Data Interpretation

14.14.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between intensities in the sample digestate and the calibration standard.

14.14.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the intensity can be determined.

14.14.1.2. Determine the concentration based on the initial calibration curve.

14.14.1.2.1. The data system is programmed to perform the calculation of concentration.

14.14.1.3. If the instrument response exceeds the calibration range, dilute the digestate and re-analyze.

14.15. Method of Standard Additions (MSA)

14.15.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.15.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition per client request or project specific DQOs.

14.15.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the acidified reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.12. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.15.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix E. A linear regression program may be used to obtain the intercept concentration.

14.15.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.15.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.15.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.15.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{I_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the intensity readings for the target analyte.
I_{ave} = mean of the intensity readings for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The slope and intercept of a linear calibration curve are calculated as follows:

$$M = \frac{I_s - I_b}{C_s - C_b} \qquad B = \frac{C_s I_b - C_b I_s}{C_s - C_b}$$

where: M = slope of the calibration curve.
B = intercept of the calibration curve.
I_s = intensity of calibration standard at a specific wavelength.
I_b = intensity of calibration blank at a specific wavelength.
C_s = concentration of calibration standard.
C_b = concentration of calibration blank.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample digestate is calculated as follows:

$$C_x = \frac{I_x - B}{M}$$

where: C_x = concentration of target analyte in digestate in mg/L.
I_x = intensity of target analyte at a specific wavelength.
B = intercept of the calibration curve.
M = slope of the calibration curve.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in mg/L.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis.

If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in g.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in g.
C_{ss} = solids content in %.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_x \times V_x \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in mg/L.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
V_{MP} = volume of mobility-procedure extract digested in mL. Unless specified otherwise, V_{MP} = 5.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.13. Refer to the preparatory method(s) for additional calculations.

15.14. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.14.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

15.15. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. ►Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the SDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective limits specified in the project specific DQO. In the absence of project specific DQO, the concentrations of target analytes in an MB should be less than or equal to the respective RLs. If regulatory limits are available, the concentrations of target analytes in an MB should be less than 10% of the respective regulatory limits. If the concentration of any target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD elements are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20% (between LCS and LCSD). All LCS (including LCSD if required) elements must be within acceptance limits (see Section 12.10.3. for additional information).

18.2.1. Refer to Section 12.10.3.1.1. for acceptance criteria if historical data is available.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD (when applicable) is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2.1. If the LCS/LCSD is used in place of the MS/MSD due to insufficient sample amount, or if LCS/LCSD is required per client or project specific DQO, both the LCS and LCSD data must be reported.

18.3. The acceptance criteria for MS/MSD elements are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20% (between MS and MSD).

18.3.1. Refer to Section 12.11.2.1.1. for acceptance criteria if historical data is available.

18.3.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

18.4.1. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are confirmed. Perform MSA (see Section 14.15.) on all samples in the same preparation batch per client request or project specific DQOs.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

18.7.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. ►The Operations Director, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the Group Leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be re-analyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 6010B, USEPA, Revision 2, December 1996.

22.2. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 6010C, USEPA, Revision 3, November 2000.

22.3. *Flame Atomic Absorption Spectrophotometry,* Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Inorganic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Recommended Wavelengths and Estimated Instrumental Detection Limits.

23.2. Appendix B: Potential Interferences (Example), Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level.

23.3. Appendix C: Standard Solution Preparation.

23.4. Appendix D: Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples.

23.5. Appendix E: Standard Addition Plot (Example).

23.6. Appendix F: Additional Quality Control Criteria for Department of Defense Projects.

23.7. Appendix G: Control Limits for Department of Defense Projects.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 6010B Revision 2 are noted.

ECI SOP M601 Section	Reference Document EPA Method 6010B Section	Summary of Modification
12.4. and 12.8.	7.4	The control limits of replicate %RSD are modified from < 5% to ≤ 5%.
12.5. and 12.9.	8.6.1.3	The acceptance criteria of ICB and CCB are modified.
12.14.	8.5.2	The spike concentration of PDS is modified from 10–100 times the IDL to 10–100 times the RL.
14.2.	7.2.5	Procedure on the determination of detection limit was modified to conform to the requirements specified in 40 CFR Part 136 Appendix B and 2009 TNI Standard.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
6.1	Entire document: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 19 and 20: Update responsibilities.	L. Hunt	2015-03-23
6.2	Section 6: Refer to QSM for the list of definitions and glossaries. Sections 8 and 17: Remove the references to MSDS. Section 9.2.2: Update the instrument software versions. Section 10.2: Add commercially prepared custom references standards. Section 19.2: Delete the reference to QA Director. Appendix F: Revise the whole appendix to conform to the DoD QSM Version 4.2. Appendix G: Revise the whole appendix to conform to the DoD QSM Version 4.2.	K. Chang	2016-05-02

Appendix A

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Eurofins Calscience, Inc.

Appendix A

Recommended Wavelengths and Estimated Instrumental Detection Limits (IDLs)

Element	Detection Wavelength [a] (nm)	Estimated IDL [b] (µg/L)
Aluminum (Al)	308.215	30
Antimony (Sb)	217.582	21
Arsenic (As)	193.696	35
Barium (Ba)	233.527	0.87
Beryllium (Be)	313.042	0.18
Boron (B)	249.677 × 2	3.8
Cadmium (Cd)	226.502	2.3
Calcium (Ca)	317.933	6.7
Chromium (Cr)	267.716	4.7
Cobalt (Co)	228.616	4.7
Copper (Cu)	324.752	3.6
Iron (Fe)	273.955	4.1
Lead (Pb)	220.353	28
Lithium (Li)	610.362	2.8
Magnesium (Mg)	279.077	20
Manganese (Mn)	257.610	0.93
Molybdenum (Mo)	202.031	5.3
Nickel (Ni)	231.604 × 2	10
Phosphorus (P)	213.617	51
Potassium (K)	766.490	See note [c]
Selenium (Se)	196.026	50
Silica (SiO2)	251.611	17
Silver (Ag)	328.068	4.7
Sodium (Na)	589.592	19
Strontium (Sr)	407.771	0.28
Thallium (Tl)	190.801	27
Tin (Sn)	189.927	17
Titanium (Ti)	336.121	5.0
Vanadium (V)	292.402	5.0
Zinc (Zn)	213.857 × 2	1.2

[a] The wavelengths listed (where ×2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 7.1.). In time, other elements may be added as more information becomes available and as required.

[b] The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c] Highly dependent on operating conditions and plasma position.

Appendix B

POTENTIAL INTERFERENCES (EXAMPLE)

Eurofins Calscience, Inc.

Appendix B

Potential Interferences (Example)

Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level [c]

Analyte		Wavelength (nm)	Interferant [ab] Al	Ca	Cr	Cu	Fe	Mg	Mn	Tl	V
Aluminum	Al	308.215	--	0.01926	0.01760	0.00290	--	0.00296	--	0.00470	0.63900
Antimony	Sb	206.836	--	--	1.50400	--	--	0.00116	--	--	--
Antimony	Sb	217.582	--	--	0.00910	--	--	0.00116	--	--	0.14900
Arsenic	As	188.979	--	--	--	0.00290	--	--	0.00440	0.00150	0.00040
Arsenic	As	193.696	--	0.00035	0.04780	--	--	--	--	--	--
Barium	Ba	233.527	0.00009	--	--	--	0.00403	0.00025	--	--	--
Beryllium	Be	313.042	--	--	0.00025	--	--	--	--	--	0.00650
Cadmium	Cd	226.502	--	--	--	--	0.00096	--	--	0.00005	0.00020
Calcium	Ca	317.933	0.00262	--	0.03450	0.00790	0.01350	0.02850	0.01330	0.00760	--
Chromium	Cr	267.716	0.00096	0.00009	--	0.02110	0.00186	0.00090	0.03080	0.00085	--
Cobalt	Co	228.616	0.00023	0.00001	--	0.00050	0.00166	0.00006	0.00045	0.00015	0.00050
Copper	Cu	324.752	0.00325	0.00229	--	--	--	0.00225	0.02680	0.04170	--
Iron	Fe	273.955	0.00617	--	0.01020	0.00660	--	0.00378	0.01140	0.00460	0.21900
Lead	Pb	220.353	--	--	--	0.00710	--	--	0.01530	0.00050	--
Magnesium	Mg	279.077	0.00066	0.00067	--	--	0.00049	--	--	0.00075	--
Manganese	Mn	257.610	--	0.00018	--	--	--	0.00041	--	0.00182	--
Molybdenum	Mo	202.031	0.00142	--	0.00625	0.00045	--	--	--	--	--
Nickel	Ni	231.604	0.00023	0.00002	0.00100	0.00010	0.00034	--	--	0.03940	0.00190
Phosphorus	P	213.617	--	--	--	0.87900	--	--	--	0.00430	0.01840
Potassium	K	766.490	--	--	--	--	--	0.00780	--	--	--
Selenium	Se	196.026	0.00667	--	--	0.00440	--	--	0.05840	--	0.00450
Silver	Ag	328.068	--	--	0.00040	0.00650	--	--	0.00045	--	--
Sodium	Na	589.592	0.09157	0.00801	0.10960	0.00580	--	0.13380	--	0.08005	--
Strontium	Sr	407.771	--	0.00258	0.00065	--	--	--	--	--	--
Thallium	Tl	190.801	0.00082	0.00378	0.04500	0.00445	0.00024	--	--	--	0.05500
Tin	Sn	189.927	0.00032	0.00301	--	0.00045	0.00059	--	0.00085	--	0.00165
Titanium	Ti	336.121	--	--	--	0.00015	0.00003	--	0.00010	0.00010	--
Vanadium	V	292.402	0.00011	--	--	--	--	0.00023	--	0.00025	--
Zinc	Zn	213.857	0.00041	0.00027	0.00285	0.05220	0.01660	0.00033	--	0.00100	--

[a] Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al	200 mg/L	Mg	200 mg/L
Ca	200 mg/L	Mn	200 mg/L
Cr	1000 mg/L	Tl	1000 mg/L
Cu	1000 mg/L	V	1000 mg/L
Fe	200 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

Appendix C

STANDARD SOLUTION PREPARATION

Eurofins Calscience, Inc.

Appendix C

Initial Calibration Standard Solution Preparation

Initial Calibration Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	200 + 2000	60 + 7.5	27	1000	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	200 + 1000	15 + 6	9	1000	
Arsenic	As	500	15	7.5	1000	
Barium	Ba	2000	7.5	15	1000	
Beryllium	Be	50 + 50	15 + 7.5	1.125	1000	
Boron	B	100 + 1000	15 + 6	7.5	1000	
Cadmium	Cd	100	15	1.5	1000	
Calcium	Ca	1000	60	60	1000	
Chromium	Cr	20	60	1.2	1000	
Cobalt	Co	500	7.5	3.75	1000	
Copper	Cu	250	7.5	1.875	1000	
Iron	Fe	1000	7.5	7.5	1000	
Lead	Pb	500	15	7.5	1000	
Magnesium	Mg	1000	15	15	1000	
Manganese	Mn	100	15	1.5	1000	
Molybdenum	Mo	200	6	1.2	1000	
Nickel	Ni	20	60	1.2	1000	
Phosphorus	P	10000	1.2	12	1000	
Potassium	K	400 + 10000	60 + 3	54	1000	
Selenium	Se	200	15	3	1000	
Silicon	Si	2000	6	12	1000	
Silver	Ag	50	15	0.75	1000	
Sodium	Na	200 + 10000	60 + 6	72	1000	
Strontium	Sr	10	60	0.6	1000	
Thallium	Tl	200	15	3	1000	
Tin	Sn	1000	6	6	1000	
Titanium	Ti	200	6	1.2	1000	
Vanadium	V	500	7.5	3.75	1000	
Zinc	Zn	100 + 10000	15 + 0.35	5	1000	
Bismuth [b]	Bi	1000	0.2	2	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	1000	0.2	2	100	
Sulfur [b]	S	1000	0.2	2	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, Li, and S standards are prepared separately.

Appendix C

Initial Calibration Verification (ICV) Standard Solution Preparation

Initial Calibration Verification (ICV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	200	4	4	200	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	200	2	2	200	
Arsenic	As	500	2	5	200	
Barium	Ba	100	2	1	200	
Beryllium	Be	50	2	0.5	200	
Boron	B	500	1	2.5	200	
Cadmium	Cd	150	2	1.5	200	
Calcium	Ca	1000	4	20	200	
Chromium	Cr	20	4	0.4	200	
Cobalt	Co	100	2	1	200	
Copper	Cu	100	2	1	200	
Iron	Fe	10000	2	100	200	
Lead	Pb	500	2	5	200	
Magnesium	Mg	1000	2	10	200	
Manganese	Mn	100	2	1	200	
Molybdenum	Mo	100 + 300	2 + 1	2.5	200	
Nickel	Ni	20	4	0.4	200	
Phosphorus	P	1000	1	5	200	
Potassium	K	400	4	8	200	
Selenium	Se	200	2	2	200	
Silicon	Si	230	1	1.15	200	
Silver	Ag	50	2	0.5	200	
Sodium	Na	200 + 10000	4 + 1	54	200	
Strontium	Sr	10	4	0.2	200	
Thallium	Tl	200	2	2	200	
Tin	Sn	10000	0.05	2.5	200	
Titanium	Ti	1000	1	5	200	
Vanadium	V	100	2	1	200	
Zinc	Zn	150	2	1.5	200	
Bismuth [b]	Bi	1000	0.1	1	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	1000	0.1	1	100	
Sulfur [b]	S	1000	0.1	1	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, Li, and S standards are prepared separately.

Appendix C

Low-Level Initial Calibration Verification (LLICV) Standard Solution Preparation

Low-Level Initial Calibration Verification (LLICV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	10000	0.5	5	1000	10% (v/v) HNO_3
Antimony	Sb	10000	0.15	1.5	1000	
Arsenic	As	10000	0.1	1	1000	
Barium	Ba	10000	0.1	1	1000	
Beryllium	Be	10000	0.1	1	1000	
Boron	B	10000	0.2	2	1000	
Cadmium	Cd	10000	0.1	1	1000	
Calcium	Ca	10000	1	10	1000	
Chromium	Cr	10000	0.1	1	1000	
Cobalt	Co	10000	0.1	1	1000	
Copper	Cu	10000	0.1	1	1000	
Iron	Fe	10000	1	10	1000	
Lead	Pb	5000 [b]	0.2	1	1000	
Magnesium	Mg	10000	1	10	1000	
Manganese	Mn	10000	0.05	0.5	1000	
Molybdenum	Mo	10000	0.1	1	1000	
Nickel	Ni	10000	0.1	1	1000	
Phosphorus	P	10000	1	10	1000	
Potassium	K	10000	5	50	1000	
Selenium	Se	10000	0.15	1.5	1000	
Silicon	Si	10000	0.5	5	1000	
Silver	Ag	10000	0.05	0.5	1000	
Sodium	Na	10000	5	50	1000	
Strontium	Sr	10000	0.3	3	1000	
Thallium	Tl	10000	0.15	1.5	1000	
Tin	Sn	10000	0.5	5	1000	
Titanium	Ti	10000	0.3	3	1000	
Vanadium	V	10000	0.1	1	1000	
Zinc	Zn	10000	0.1	1	1000	
Bismuth [b]	Bi	1000	1	10	100	5% (v/v) HNO_3
Lithium [b]	Li	1000	0.5	5	100	
Sulfur [b]	S	1000	1	10	100	
Lead	Pb	10000	100	5000	200	H_2O

[a] HNO_3 is concentrated trace metals grade acid.

[b] Bi, Li, and S standards are prepared separately; 5000-ppm Pb standard is prepared separately.

Appendix C

Continuing Calibration Verification (CCV) Standard Solution Preparation

Continuing Calibration Verification (CCV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	27	50	13.5	100	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	9	50	4.5	100	
Arsenic	As	7.5	50	3.75	100	
Barium	Ba	15	50	7.5	100	
Beryllium	Be	1.125	50	0.5625	100	
Boron	B	7.5	50	3.75	100	
Cadmium	Cd	1.5	50	0.75	100	
Calcium	Ca	60	50	30	100	
Chromium	Cr	1.2	50	0.6	100	
Cobalt	Co	3.75	50	1.875	100	
Copper	Cu	1.875	50	0.9375	100	
Iron	Fe	7.5	50	3.75	100	
Lead	Pb	7.5	50	3.75	100	
Magnesium	Mg	15	50	7.5	100	
Manganese	Mn	1.5	50	0.75	100	
Molybdenum	Mo	1.2	50	0.6	100	
Nickel	Ni	1.2	50	0.6	100	
Phosphorus	P	12	50	6	100	
Potassium	K	54	50	27	100	
Selenium	Se	3	50	1.5	100	
Silicon	Si	12	50	6	100	
Silver	Ag	0.75	50	0.375	100	
Sodium	Na	72	50	36	100	
Strontium	Sr	0.6	50	0.3	100	
Thallium	Tl	3	50	1.5	100	
Tin	Sn	6	50	3	100	
Titanium	Ti	1.2	50	0.6	100	
Vanadium	V	3.75	50	1.875	100	
Zinc	Zn	5	50	2.5	100	
Bismuth [b]	Bi	2	50	1	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	2	50	1	100	
Sulfur [b]	S	2	50	1	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, Li, and S standards are prepared separately.

Appendix C

Interference Check Standard AB (ICS-AB) Solution Preparation

Interference Check Standard AB (ICS AB)						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	1200	10	24	500	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	500	1	1	500	
Arsenic	As	1000	0.5	1	500	
Barium	Ba	300	0.5	0.3	500	
Beryllium	Be	100	0.5	0.1	500	
Boron	B	500	0.5	0.5	500	
Cadmium	Cd	300	0.5	0.3	500	
Calcium	Ca	6000	10	120	500	
Chromium	Cr	300	0.5	0.3	500	
Cobalt	Co	300	0.5	0.3	500	
Copper	Cu	300	0.5	0.3	500	
Iron	Fe	5000	10	100	500	
Lead	Pb	1000	0.5	1	500	
Magnesium	Mg	3000	10	60	500	
Manganese	Mn	200	0.5	0.2	500	
Molybdenum	Mo	300	0.5	0.3	500	
Nickel	Ni	300	0.5	0.3	500	
Phosphorus	P					
Potassium	K	20000	0.5	20	500	
Selenium	Se	500	0.5	0.5	500	
Silicon	Si	200	0.5	0.2	500	
Silver	Ag	300	0.5	0.3	500	
Sodium	Na	1000	10	20	500	
Strontium	Sr					
Thallium	Tl	1000	0.5	1	500	
Tin	Sn					
Titanium	Ti	1000	0.5	1	500	
Vanadium	V	300	0.5	0.3	500	
Zinc	Zn	300	0.5	0.3	500	
Bismuth	Bi					
Lithium	Li					
Sulfur	S					

[a] HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Interference Check Standard A (ICS-A) Solution Preparation

Interference Check Standard A (ICS A)						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	1200	10	24	500	5% (v/v) HCl + 6% (v/v) HNO_3
Calcium	Ca	6000	10	120	500	
Iron	Fe	5000	10	100	500	
Magnesium	Mg	3000	10	60	500	
Sodium	Na	1000	10	20	500	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

Internal Standard Solution Preparation

Internal Standard						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Holmium	Ho	10000	1	5	2000	5% (v/v) HCl + 6% (v/v) HNO_3
Terbium	Tb	10000	1	5	2000	
Yttrium	Y	10000	1	5	2000	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Spike Standard Solution Preparation

Spike Standards 1 & 2						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	10000	10	100	1000	10% (v/v) HNO_3
Antimony	Sb	10000	10	100	1000	
Arsenic	As	10000	10	100	1000	
Barium	Ba	10000	10	100	1000	
Beryllium	Be	10000	10	100	1000	
Boron	B	10000	10	100	1000	
Cadmium	Cd	10000	10	100	1000	
Calcium	Ca	10000	10	100	1000	
Chromium	Cr	10000	10	100	1000	
Cobalt	Co	10000	10	100	1000	
Copper	Cu	10000	10	100	1000	
Iron	Fe	10000	10	100	1000	
Lead	Pb	5000 [b]	20	100	1000	
Magnesium	Mg	10000	10	100	1000	
Manganese	Mn	10000	10	100	1000	
Molybdenum	Mo	10000	10	100	1000	
Nickel	Ni	10000	10	100	1000	
Phosphorus	P	10000	10	100	1000	
Potassium	K	10000	100	1000	1000	
Selenium	Se	10000	10	100	1000	
Silicon	Si	10000	10	100	1000	
Silver	Ag	10000	5	50	1000	
Sodium	Na	10000	100	1000	1000	
Strontium	Sr	10000	10	100	1000	
Thallium	Tl	10000	10	100	1000	
Tin	Sn	10000	10	100	1000	
Titanium	Ti	10000	10	100	1000	
Vanadium	V	10000	10	100	1000	
Zinc	Zn	10000	10	100	1000	
Bismuth [b]	Bi	1000	20	200	100	5% (v/v) HNO_3
Lithium [b]	Li	1000	20	200	100	
Sulfur [b]	S	1000	20	200	100	
Lead	Pb	10000	100	5000	200	H_2O

[a] HNO_3 is concentrated trace metals grade acid.

[b] Bi, Li, and S standards are prepared separately; 5000-ppm Pb standard is prepared separately.

Appendix D

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Eurofins Calscience, Inc.

Appendix D

Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples

Measurement		Digestion Volume (mL) [a, c]	Collection Volume (mL) [a, c]	Treatment/Preservative Holding Time [b]
Inorganic Analytes (except hexavalent chromium and mercury):				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 6 months
	Dissolved	50	250	Filter on site HNO_3 to pH < 2 6 months
	Suspended	50	250	Filter on site 6 months
Solid				
	Total	2 g	4 oz	6 months
Hexavalent Chromium:				
Aqueous		50	250	24 hours Store at 4 ± 2°C until analyzed
Solid		2.5 g	4 oz	1 month to extraction 4 days after extraction Store at 4 ± 2°C until analyzed
Mercury:				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 28 days
	Dissolved	50	250	Filter HNO_3 to pH < 2 28 days
Solid				
	Total	0.2 g	4 oz	28 days Store at 4 ± 2°C until analyzed

[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

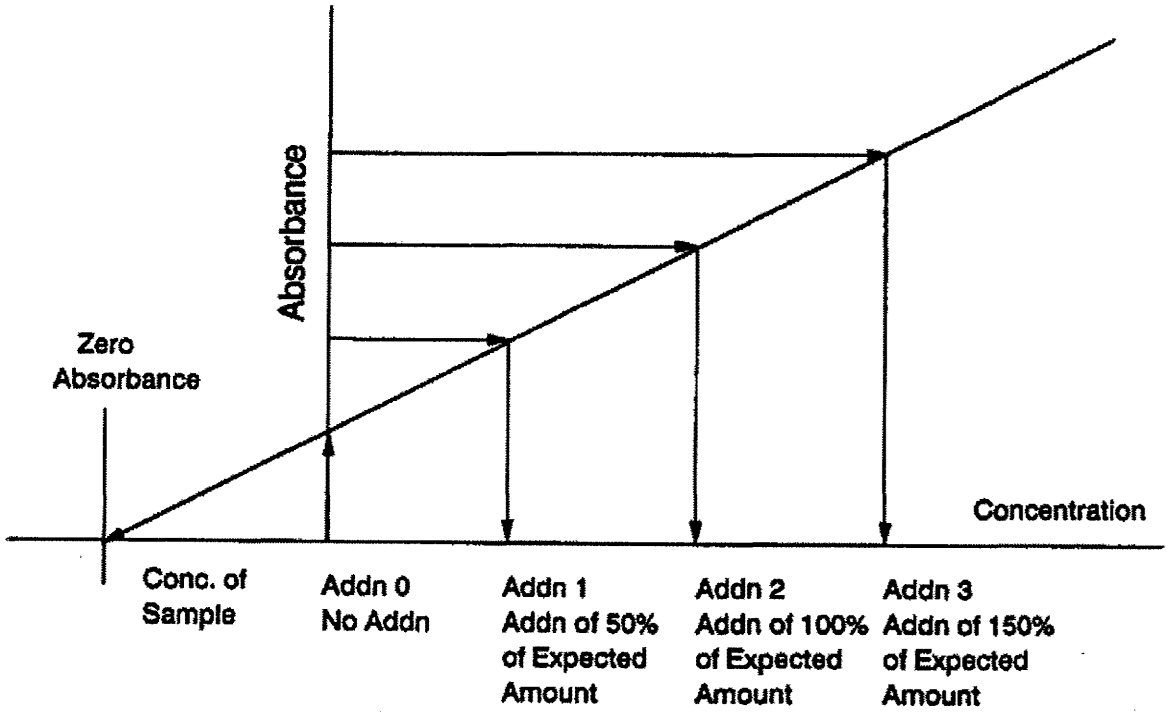
Appendix E

STANDARD ADDITION PLOT (EXAMPLE)

Eurofins Calscience, Inc.

Appendix E

Standard Addition Plot (Example)



Appendix F

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 6010B, Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. DETECTION / QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. ►STANDARDS

4.1. Initial Calibration Verification (ICV)

4.1.1. The concentration of the ICV standard shall be at or near the midpoint of the calibration range.

4.2. Low-Level Initial Calibration Verification (LLICV) Solution

4.2.1. Prepare the LLICV working standard solutions by diluting the appropriate volumes of the stock standards and concentrated HNO_3 to the specified volumes with reagent water.

4.2.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the LLICV working standard solutions.

4.2.3. Dilute the appropriate volumes of the LLICV working standard solution with reagent water for low-level initial calibration verification.

4.2.3.1. Each target analyte in the LLICV solution is at a concentration expected to be the LOQ.

4.2.4. Prepare the LLICV solution fresh daily.

4.2.5. The LLICV solution is of a source same as that used for the initial one-point calibration.

4.2.6. The concentration of the LLICV standard shall be less than or equal to the LOQ.

4.3. Continuing Calibration Verification (CCV)

4.3.1. The concentration of the CCV standard shall be ***between*** the low calibration standard and the midpoint of the calibration range.

4.4. The use of a standard from a second lot ***as a second source standard is acceptable when only one manufacturer of the standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.***

5. ►QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. Detection limit (DL) determination shall be performed for each analyte at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following each DL determination and quarterly thereafter.

5.1.2.1. LOD verification sample shall be prepared by spiking a quality system matrix at ***approximately 2 to 3 times the DL (for a single-analyte standard) or greater than 1 to 4*** times the DL ***(for a multi-analyte standard)***.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise (S/N) ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the DL determination and LOD verification ***at a higher concentration***.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the calibration range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ for each analyte.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking a quality system matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The LOQ and the calibration standard establish the quantitation range which must lie within the linear dynamic range.

5.3.1.1. When sample results exceed the quantitation range, dilute and re-analyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.

5.4. Low-Level Initial Calibration Verification (LLICV)

5.4.1. Immediately following the analysis of an ICV standard, an LLICV standard must be analyzed prior to sample analysis.

5.4.2. The ***accuracy of measurements at or near the RL is confirmed if*** the %D for each analyte is ≤ 20%.

5.4.3. If these criteria are not met, ***no sample analysis shall begin. Effect corrective action and re-analyze the LLICV.***

5.5. Initial Calibration Blank (ICB)

5.5.1. Immediately following the analysis of an LLICV standard, an ICB must be analyzed prior to sample analysis.

5.5.2. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > LOD.

5.5.3. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and re-analyze the ICB.

5.6. Daily Spectral Interference Check (ICS-AB and ICS-A)

5.6.1. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A solutions must be analyzed daily prior to sample analysis.

5.6.2. The ICS-AB is deemed acceptable if the %D for each analyte is ≤ 20%.

5.6.3. The ICS-A is deemed acceptable if the absolute value of the concentration for each non-spiked analyte is < LOD (unless it is a verified trace impurity from one of the spiked analytes).

5.6.4. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and re-analyze the ICS-AB and/or ICS-A.

5.7. Continuing Calibration Verification (CCV)

5.7.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 field samples or portion thereof within a 24-hour shift, and at the end of sequence.

5.7.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

5.7.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. ***Effect corrective action*** and re-analyze the CCV.

5.7.3.1. If the ***CCV remains unacceptable***, recalibrate and re-analyze all samples since the last acceptable CCV.

5.8. Continuing Calibration Blank (CCB)

5.8.1. Immediately following the analysis of a CCV standard, a CCB must be analyzed prior to sample analysis.

5.8.2. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > LOD.

5.8.3. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and re-analyze the CCB. Re-analyze all samples since the last acceptable CCB.

5.8.3.1. ***The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed CCB.***

5.9. Event Based Quality Control (MBs and LCS/LCSDs)

5.9.1. Method Blanks (MBs)

5.9.1.1. The MB shall be considered to be contaminated if one of the following conditions is met.

5.9.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the ***RL***, and is greater than 1/10 the amount measured in any associated sample or 1/10 the regulatory limit (whichever is greater).

5.9.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds ***RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater)***.

5.9.1.1.3. ***The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs)***.

5.9.1.2. If the MB is contaminated, re-process the affected samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.9.1.2.1. If insufficient sample volume remains for re-processing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.9.2. Laboratory Control Samples (LCS/LCSDs)

5.9.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element in aqueous and solid matrices are listed in Appendix G.

5.9.2.2. All reported analytes must be spiked. The concentration of each spike analyte shall be at or below the midpoint of the calibration if project specific concentration is not specified.

5.9.2.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.9.2.3.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.

5.9.2.4. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.10. Matrix Based Quality Control (MS/MSDs)

5.10.1. Matrix Spikes (MS/MSDs)

5.10.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in aqueous and solid matrices are listed in Appendix G. The RPD is ≤ 20% ***(between MS and MSD)***.

5.10.1.2. All reported analytes must be spiked. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5.10.1.3. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.10.1.3.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on

historical data with at least 30 data points generated under the same analytical process.

5.11. Dilution Test

5.11.1. If ***an analyte concentration*** is > 50 × LOQ, prepare a dilution test sample per preparation batch per matrix with a 1:5 dilution.

5.11.2. The analyte concentration in the dilution test sample must be within ± 10% of the original determination.

5.11.3. If this criterion is not met, ***perform post digestion spike addition***.

5.12. Post Digestion Spike (PDS) Addition

5.12.1. If ***the dilution test fails or an analyte concentration in all samples*** is < 50 × ***LOD***, prepare a PDS sample per preparation batch per matrix.

5.12.2. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10–100 times the LOQ.

5.12.3. The acceptance criteria for PDS elements are as follows:

5.12.3.1. The lower and upper acceptance limits for %REC of each PDS element are ***75%*** and ***125%***, respectively.

5.12.3.2. If these criteria are not met, ***perform MSA on all samples in the same preparation batch***.

6. ►PROCEDURE

6.1. Following the establishment of a valid initial calibration, an LLICV standard must be analyzed daily immediately following ICV.

6.1.1. If LLICV fails, effect corrective action prior to analyzing any samples.

6.2. Blank, standard, and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard
3) Initial Calibration Verification (ICV)
4) Low-Level Initial Calibration Verification (LLICV)
5) Initial Calibration Blank (ICB)
6) Interference Check Solution AB (ICS-AB)
7) Interference Check Solution A (ICS-A)
8) Continuing Calibration Verification (CCV)
9) Continuing Calibration Blank (CCB)
10) Method Blank (MB)
11) Laboratory Control Samples (LCS)
12) Laboratory Control Sample Duplicates (LCSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Matrix Spike (MS)

15) Matrix Spike Duplicate (MSD)
16) Dilution Test Sample
17) Post Digestion Spike (PDS)
18) Ending CCV
19) Ending CCB

6.2.1. Item 4: An LLICV is a standard used to confirm the accuracy of measurement at or near the ***RL***. An acceptable LLICV is required daily immediately following ICV.

6.2.2. Item 5: The ICB is an aliquot of acidified reagent water used to monitor contamination. An acceptable ICB is required immediately following LLICV.

6.2.3. Item 16: The dilution test sample is prepared from the five-fold dilution of a sample ***with an analyte concentration greater than 50 × LOQ*** post digestion. The sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

6.2.3.1. One dilution test sample is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

6.2.4. Item 17: The PDS is the same sample matrix from which the MS/MSD samples were prepared or from another sample in the same preparation batch, and is spiked with known concentrations of specific target analytes post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

7. REFERENCES

7.1. ►Department of Defense Quality Systems Manuals for Environmental Laboratories, Version ***4.2, October 2010***.

Appendix G

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECTS

Eurofins Calscience, Inc.

Appendix G

DoD Control Limits of LCS/LCSD/MS/MSD Elements in Aqueous Matrix

Analyte		Control Limit		ME Limit	
		Lower	Upper	Lower	Upper
Aluminum	Al	80	120	80	120
Antimony	Sn	80	120	80	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Chromium	Cr	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	80	120	75	120
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	80	120

Note: ME limits are applicable to LCS/LCSD elements only.

Appendix G

DoD Control Limits of LCS/LCSD/MS/MSD Elements in Solid Matrix

Analyte		Control Limit		ME Limit	
		Lower	Upper	Lower	Upper
Aluminum	Al	80	120	75	120
Antimony	Sn	80	120	75	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Chromium	Cr	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	75	120	70	125
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	75	120

Note: ME limits are applicable to LCS/LCSD elements only.

Title : **EPA METHOD 7199, DETERMINATION OF HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY**

Document No. : SOP-M737
Revision No. : 2.0
Supersedes : 1.4

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PROPRIETARY INFORMATION STATEMENT

Revision 2.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 06/10/15
MANAGEMENT **DATE**

_____ 06-10-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 7199, Determination of Hexavalent Chromium by Ion Chromatography.

2. ►APPLICABLE MATRICES

2.1. Method 7199 is applicable for the determination of hexavalent chromium in drinking water, ground water, industrial wastewater effluents, and solid waste extracts.

2.2. ***Solid samples may be reported using this method. Solid samples must first be prepared using EPA 3060A, Alkaline Digestion, prior to analysis.***

3. ►DETECTION / QUANTITATION LIMITS

3.1. The standard reporting limits (RLs) for this method are 1.0 µg/L in aqueous matrices and 40 µg/kg in solid matrices.

3.1.1. ***The low-level aqueous reporting limit is 0.02 ug/L.***

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography (IC) and skillful in the interpretation of chromatographic data.

4.2. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for solid samples.

5. ►METHOD SUMMARY

5.1. An aqueous sample is filtered through a 0.45-µm filter ***(in some cases further filtration through a 0.2-µm filter is necessary, especially for alkaline digestates)***, and the filtrate is adjusted to a pH = 9.0−9.5 with a buffer solution.

5.2. A measured volume of the sample (250 µL ***or 1000 µL***) is introduced into the ion chromatograph. The sample is passed through a guard column that removes organics from the sample ***before the Cr(VI) as CrO is separated on an anion exchange separator column (analytical column)***. Hexavalent chromium then undergoes post column derivitization with 1,5-diphenylcarbazide to form a highly colored complex that is detected at 530 nm.

5.3. Solid samples are extracted using EPA 3060A, which involves alkaline digestion of the solid materials, prior to analysis by EPA 7199. Please refer to SOP-M224 for information on the alkaline digestion procedure.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.2.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.2.2. ***A filtration batch is composed of one to 20 aqueous environmental samples filtered at the same time using the same batch of filters and syringes. The associated quality control (MB and LCS, MS, etc.) must be prepared at the same time and be treated in the same manner as the field samples. The filtration procedure must be documented so as to allow for the traceability and linking of the initial analyses, dilution analyses, and QC analyses together.***

6.2.2.1. ***Filtrates, if maintained in appropriate condition (i.e., covered container) and at the appropriate temperature (i.e., refrigerated if not in use) may be used for both initial and dilution analyses, as applicable to the sample and any target analytes present within.***

6.2.2.2. ***In the above case, filtration batches may be associated with the same set of QC samples (MB and LCS, MS, etc.) even if analyzed on different days.***

6.2.2.3. ***If a new filtered aliquot must be generated for dilution analysis, all applicable QC (MB, LCS/LCSD or LCS/MS/MSD) must also be prepared and a new batch created.***

6.2.3. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.3. Continuing Calibration Verification (CCV): ***Also known as the Instrument Performance Check (IPC) Sample.***

6.4. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised.

6.5. Initial Calibration Verification (ICV): ***Also known as the Quality Control Sample (QCS).*** An uncontaminated sample matrix spiked with known concentrations of analytes from a source independent from the calibration standards.

6.6. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.7. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.8. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.9. Method Blank: A sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.10. ***Quality Control Sample (QCS): Also known as the ICV. Obtained and prepared from an independent source (EPA, NIST, or from a commercial source). Dilute an aliquot according to the instructions and analyze with samples. If an EPA or NIST reference sample is not available, a mid-range standard, prepared from an independent commercial source, may be used.***

6.11. ***Refer to the current version of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. ►INTERFERENCES

7.1. ***Samples containing high levels of potassium permanganate may interfere with the accurate quantitation of hexavalent chromium and may lead to biased high results. This interference appears to be due to a reaction of permanganate with the post-column reagent that gives a colored species with much less absorbance at 530 nm than either permanganate itself or the complex of chromium species with the post-column reagent.***

7.1.1. ***Samples containing high levels of permanganate may be effectively treated with ascorbic acid. However, the amount of ascorbic acid should not exceed more than 1000 mg/L due to potential negative effects on the instrumentation.***

7.2. ***Samples containing high levels of organic materials and/or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). In addition, reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. However, at a pH of 6.5 or greater, CrO_4^{2-}, which is less reactive than the $HCrO_4^-$, is the predominant species.***

7.3. ***Samples containing high levels of anionic species such as sulfate and chloride can result in loss of Cr(VI) due to column overload. Poor recoveries from spiked samples and tailing peaks are typical manifestations of column overload.***

7.4. ***Contamination may come from trace amounts of Cr which is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess for potential Cr(VI) contamination. Contamination may also be a result of improperly cleaned glassware or contact with caustic or acidic reagents of samples with stainless steel or pigmented material.***

7.5. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.6. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated chromatographic baseline.

7.7. Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. ***Soil samples shall be filtered through a 0.45-µm filter followed by a 0.2-µm filter prior to analysis.***

8. ►SAFETY

8.1. ***Hexavalent chromium is toxic and is a suspected human carcinogen where exposure may result in lung or other forms of cancer. For this reason, the inorganic salt must be handled with extreme care when weighing out standards or when handling the aqueous form, whether standards or samples.***

8.2. ***The salt form should be handled in a hood to avoid accidental exposure through inhalation and/or ingestion. If inhaled, remove to fresh air and seek medical attention as needed. If ingested, do not induce vomiting and seek immediate medical attention.***

8.3. ***Skin exposure to the salt or liquid form may cause skin irritation and/or a more intense allergic reaction resulting in a rash. Thoroughly wash all exposed areas with soap and water and rinse thoroughly. Seek medical attention should the rash intensify.***

8.4. ***Be sure to wear proper eye protection at all times and remove and properly separate soiled lab coats or other contaminated clothing in the event of splashing or spills.***

8.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling samples and chemicals.

8.6. Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the SDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Ion Chromatograph:

9.1.1. Dionex DX-500, DX-600, ICS-3000, ICS-5000, or equivalent Ion Chromatograph configured with a post-column reagent delivery module and an autosampler.

9.1.2. Eluent Pump: capable of withstanding a minimum backpressure of 2000 psi and of delivering a constant flow in the range of ***0.3***–5mL/min.

9.1.3. Sample Loop: 250 µL ***(regular level)*** or 1000 µL ***(low level)***.

9.1.3.1. ***The flow rate, after the absorbance detector, is set at approximately 0.35 mL/min for the low-level analysis and between 1.0 and 2.0 mL/min for the regular level analysis.***

9.1.4. Detector: Absorbance.

9.1.5. Analytical Column: Dionex IonPac AS7, 4-mm or equivalent ***for regular level reporting and 2-mm for low-level reporting.***

9.1.6. Guard Column: Dionex IonPac NG1, 4-mm or equivalent ***for regular level reporting and 2-mm for low-level reporting.***

9.2. Instrument Software

9.2.1. Requires a PC-based data system or equivalent.

9.2.2. Dionex Chromeleon version 6.80 or Peaknet version 6.4, or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. ***Preventive maintenance should be performed at least annually and should involve the following:***

9.3.1.1. ***Rebuilding the injection valve and the auxiliary valves.***

9.3.1.2. ***Replacing the pump check valves.***

9.3.1.3. ***Replacing the pump piston rinse seals and piston seals.***

9.3.1.4. ***Replacing the waste valve and priming valve O-rings.***

9.3.1.5. ***Replacing the end-line filter.***

9.3.2. Additional information can be found in the user manual or operating guide for the specific ***Dionex*** instrument.

9.3.3. Refer to the current revision of SOP-T066 for additional instrument maintenance and troubleshooting***, as needed***.

9.4. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.5. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.6. Ultra high purity helium.

9.7. Volumetric flasks, 10 mL, 100 mL, and 1000 mL, or other volumes as needed, Class A.

9.8. ***Calibrated*** pipetters, 0.1 mL, 1 mL, 10 mL, or other volumes as needed.

9.9. Magnetic stirrer and stir bars, Teflon coated, for standard preparation.

9.10. pH meter, capable of an accuracy reading of ± 0.03 pH units.

9.11. pH paper, narrow-range, pHydrion Controls 9.0 to 10.0, or equivalent.

9.12. Transfer pipets, disposable.

9.13. Erlenmeyer flasks, 125 mL or other volumes as needed.

9.14. Sample Filtration Device.

9.14.1. Disposable syringes, 10 mL, luer-lock.

9.14.2. Syringe filter disks, 0.45 µm, luer-lock.

9.14.3. ***Syringe filter disks, 0.2 µm, luer-lock.***

9.15. ***Specimen Cups – 125 mL, with cap.***

9.16. Beakers, 50 mL, 100 mL, 500 mL, or other volumes as needed.

9.17. Graduated cylinders, 50 mL, 100 mL, 500 mL, or other volumes as needed.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water: Ultrapure water having a conductivity ≥ 18 MΩ.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Ammonium sulfate, $(NH_4)_2SO_4$, reagent grade or equivalent.

10.1.4. Ammonium hydroxide, NH_4OH, 28–30%, reagent grade or equivalent.

10.1.5. Eluent Solution: 250-mM $(NH_4)_2SO_4$ and 100-mM NH_4OH.

10.1.5.1. In a 1000-mL volumetric flask, dissolve 33.00 ± 0.33 g ammonium sulfate in 500 mL reagent water and add 6.5 mL ammonium hydroxide. Dilute to final volume (1000 mL) with reagent water and degas with helium for 10 minutes. The eluent must be prepared fresh as needed.

10.1.6. 1,5-diphenylcarbizide, $C_{13}H_{14}N_4O$, reagent grade or equivalent.

10.1.7. Methanol, CH_3OH, HPLC grade or equivalent.

10.1.8. Sulfuric acid, H_2SO_4, concentrated, reagent grade or equivalent.

10.1.9. Post-column reagent:

10.1.9.1. In a 1000-mL volumetric flask, dissolve 0.5000 ± 0.005 g 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. In a 1000-

mL beaker or flask, add 28 mL 98% sulfuric acid to 500 mL reagent water, mix, and degas with helium for 10 minutes. Once degassing is completed, add the H_2SO_4 solution to the diphenylcarbazide solution and then dilute to final volume (1000 mL) with reagent water. The post column reagent must be prepared fresh every 3 days, if not sooner, due to stability issues.

10.1.10. Buffer solution:

10.1.10.1. In a 100-mL volumetric flask, dissolve 3.30 ± 0.03 g ammonium sulfate in 75 mL reagent water and add 6.5 mL ammonium hydroxide. Dilute to final volume (100 mL) with reagent water.

10.1.11. Potassium dichromate, $K_2Cr_2O_7$, reagent grade or equivalent.

10.1.12. Matrix pretreatment cartridges in the barium form: (Dionex OnGuard II Ba cartridges, P/N 057093, or equivalent.) These cartridges are conditioned according to the manufacturer's directions.

10.1.13. Matrix pretreatment cartridges in the silver form: (Dionex OnGuard II Ag cartridges, P/N 057089, or equivalent.) These cartridges are conditioned according to the manufacturer's directions.

10.1.14. Matrix pretreatment cartridges in the hydrogen form: (Dionex OnGuard II H cartridges, P/N 057085, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce cations in the sample matrix. This protects the analytical column by removing silver or barium that has leached from the Ag or Ba cartridges.

10.1.15. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. ***Stock Standard: Inorganic Salts***

10.2.1.1. ***Potassium dichromate*** ($K_2Cr_2O_7$): ***Fisher # P188-500 or J.T. Baker # 3090-01, or equivalent.***

10.2.1.2. ***Intermediate*** standards are prepared by first drying the inorganic salts for 1 hour in a drying oven at 103−105°C. After drying, cool to ambient temperature in a desiccator. ***Inorganic salts should be stored in a desiccator when not in use.***

10.2.2. ***Intermediate Standard: 1000 ppm Hexavalent Chromium***

10.2.2.1. To make the 1000-ppm ***intermediate*** solution, weigh 0.2829 ± 0.0028 g ***potassium dichromate*** ($K_2Cr_2O_7$) into a 100-mL volumetric flask and dilute to ***100 mL*** with reagent water. Stopper the flask and invert three times. Store the intermediate solution under refrigeration when not in use.

10.2.2.1.1. If the salts won't go readily into solution, place a small stir bar into the flask, stopper, and place on a

magnetic stirrer until the salts have dissolved. ***Add the stir bar after bringing to volume.***

10.2.2.2. ***Prepare the 1000-ppm intermediate standard fresh every six months.***

10.2.2.2.1. ***The expiration date is 6 months from preparation date unless the manufacturer's date on the inorganic salt is less than this time period; if so, then the manufacturer's date will take precedence for the intermediate and all working solutions.***

10.2.2.3. ***Repeat this same process for the second source standard.***

10.2.3. ***Working standard: 10 ppm Hexavalent Chromium***

10.2.3.1. Prepare a 10-ppm ***(10,000-ppb)*** working standard by diluting 0.50 mL of the 1000-ppm ***intermediate*** standard to a final volume of 50 mL with reagent water.

10.2.3.2. ***Alternatively, the working standard is prepared gravimetrically by weighing exactly 100.0 g of reagent water into a specimen cup. Quickly remove exactly 1.0 mL of the water using a calibrated pipetter. Then add exactly 1.0 mL of the 1000-ppm intermediate standard to the specimen cup using a calibrated pipetter.***

10.2.3.3. ***Cap tightly and invert 3 times to mix. This will result in a 10-ppm working standard.***

10.2.3.3.1. ***This expiration date on the 10-ppm working solution is 6 months, earlier if the manufacturer's date is less.***

10.2.3.3.2. ***Prepare calibration, verification, and spiking standards from this working standard using calibrated pipetters and serial dilution, as noted below.***

10.2.3.4. ***Repeat this same process for the second source standard.***

10.2.3.5. Initial Calibration Standards:

10.2.3.5.1. Initial Calibration standards are prepared by diluting the appropriate amounts of the working standard with reagent water and buffer solution.

Standard Concentration (ppb)	Final Volume (mL)	Initial Concentration (ppb)	Initial Volume (mL)	Buffer Volume (mL)
100	100	10000	1.0	1.0
50	50	100	25	0.50
10	100		10	1.0
5.0	10		0.50	0.10
1.0			0.10	
0.20			0.020	
0.05*		1.0	0.50	
0.02*			0.20	

Calibration levels 0.02 ppb and 0.05 ppb are only analyzed if low-level reporting (RL = 0.02) is required. In this case, the instrument must be set up with the 1000-µL loop and the 2-mm column. If this is not the case, then these standards are not required and the low calibration point for routine hexavalent chromium analysis is 0.2 ppb (RL = 0.2 ppb).

10.2.3.5.2. ***Calibration standards must be prepared fresh on the day of use.***

10.2.3.6. Initial and Continuing Calibration Verification (ICV/CCV) solutions and Spiking Solution

10.2.3.6.1. Prepare the ICV solution by diluting 0.50 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water. ***This same solution will be used as the spiking solution for the LCS and MS/MSD (see 10.2.4.2.).***

10.2.3.6.2. Prepare CCV solutions by diluting 0.50 mL of the 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water.

10.2.3.6.3. Prepare ICV solutions for low-level analysis by diluting 0.10 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water.

10.2.3.6.4. Prepare CCV solutions for low-level analysis by diluting 0.10 mL of the 10-ppm working standard and 1.0 L of buffer to a final volume of 100 mL with reagent water.

10.2.3.6.5. ***Standards may be prepared in volumetric flasks or via the gravimetric approach.***

10.2.4. Spiking Solution / Second Source Standards:

10.2.4.1. Second-source standards will be used to prepare the Initial Calibration Verification (ICV), Laboratory Control Sample (LCS), and Matrix Spike (MS) solutions

10.2.4.2. ***10-ppm Spiking Solution***

10.2.4.2.1. Prepare the spiking solution by diluting 0.50 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water. This solution will be used to spike the LCS and MS/MSD.

10.2.4.2.2. Prepare LCS solutions for low-level analysis by diluting 0.10 mL of the second-source 10-ppm working standard and 1.0 mL of buffer to a final volume of 100 mL with reagent water.

10.2.4.2.3. ***Standards may be prepared in volumetric flasks or via the gravimetric approach.***

10.2.5. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.3. Solutions may be prepared in final volumes other than those noted, provided that correct ratios of all components are maintained.

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL HDPE containers with Teflon-lined lids.

11.2. Soil samples should be collected in 2-ounce clear wide mouth jars with Teflon-lined closures, or other glass or plastic container that does not contain stainless steel.

11.3. Samples should be maintained in a chilled state, 0–6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions.

11.4. Bring to ambient temperature prior to analysis.

11.5. Aqueous samples must be analyzed within 24 hours after collection.

11.6. ***Solid samples must digested using EPA 3060A within 30 days from collection. (Hexavalent chromium has been shown to be quantitatively stable in field-moist solid samples for 30 days after collection.)***

11.6.1. ***Following digestion samples must either be stored under dark and refrigerated (0–6°C) conditions and must be analyzed within a 7-day period post digestion, or must go directly to analysis where a holding time of 24 hours would apply if maintained at ambient temperature.***

12. ▶QUALITY CONTROL

12.1. ***Method Detection Limit Study:***

12.1.1. ***A valid MDL study must be performed prior to sample processing.***

12.1.2. ***The MDL must be verified initially, immediately following the MDL study and then again annually for NELAC. A quarterly DL verification must be performed for DOD work.***

12.1.3. ***The MDL must be repeated for any major changes to the instrumentation or when the column is replaced, if an MDL verification standard does not support the current MDL (loss of sensitivity).***

12.1.4. ***Refer to the current version of SOP-T006 for further information regarding the MDL/DL process.***

12.2. ***Initial Demonstration of Capability***

12.2.1. ***All analysts must participate in an initial demonstration of capability (IDOC) and successfully meet the requirements in order to process and report data on their own. These requirements must be met at a minimum of annually with the processing of a continuing demonstration of capability (CDOC)***

12.2.2. ***Analysts without a current IDOC or CDOC are not allowed to report data without direct oversight by a senior chemist or group leader.***

12.3. ***DL/LOD/LOQ Study for DOD Samples***

12.3.1. ***A valid Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ) study shall be performed prior to the analysis of DOD samples. Please refer to section 7.6 and to the current version of SOP T006, Appendix A for further information on the processing of the DL/LOD/LOQ study.***

12.4. ***QC Criteria Overview***

QC Element	Frequency	Acceptance Criteria	Corrective Action Section
Multipoint ICAL	Initially, prior to sample or QC analysis. As needed thereafter, and at least annually	r = 0.995 or r^2 = 0.990	12.5.1
ICV / CCV	ICV: Immediately following the ICAL standards CCV: Daily/Opening, bracketing every 10 samples, and at the end of the sequence.	ICV and CCV: +/- 10%D	12.5.2. / 12.5.4.
ICB / CCB	ICB: Immediately following the ICV CCB: Immediately following the CCV, throughout the sequence.	ICB and CCB: ND ≤ MDL/DL	12.5.3. / 12.5.5.

RT Window	Establish initially and then update daily with first CCV/midpoint ICAL standard.	Analyte retention time must fall within defined window.	12.6.
Method Blank	1 per batch of 20 samples	ND < ½ RL or < ½ LOQ (DOD)	12.7.
LCS	1 per batch of 20 samples (LCS/LCSD if insufficient volume for the MS/MSD)	% REC: 80% – 120% % RPD: 20% (LCS/LCSD)	12.8.
MS/MSD	1 pair per batch of 20 samples	Water: % REC: 70% – 130% Soil: % REC: 75% – 125% % RPD: 25%	12.9.

12.5. Instrument Calibration

12.5.1. Multi-point Initial Calibration (ICAL):

12.5.1.1. The instrument must be properly calibrated prior to the processing of sample extracts. ***This is done by analyzing a calibration blank and then 6 sequential points in order of increasing concentration (8 points if low-level analysis is performed).***

12.5.1.2. The initial calibration is assumed to be valid with a correlation coefficient (r) of 0.999 or greater, or a coefficient of determination (r^2) of 0.998 or greater. ***This criterion is applicable to all samples and projects including DOD work.***

12.5.1.3. If this criterion is not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and re-calibrate.

12.5.2. Initial Calibration Verification (ICV):

12.5.2.1. Following the analysis of the initial calibration standards an initial calibration verification (ICV) standard must be analyzed.

12.5.2.2. The ICV is deemed acceptable if the %D is ≤ 10%. ***This criterion is applicable to all samples and projects including DOD work.***

12.5.2.2.1. If this criterion is not met, the initial calibration is deemed unacceptable for sample analysis to begin.

12.5.2.2.2. ***Effect corrective action and reprepare/reanalyze a new ICV aliquot to confirm the recovery. If the ICV still fails to meet acceptance criteria, recalibrate the instrument. The second ICV analysis must be performed prior to the analysis of any samples or QC elements.***

12.5.2.2.3. ***If samples or QC have been analyzed (say, a sequence was run overnight), then the instrument must be recalibrated and validated***

with a passing ICV and all samples reanalyzed against the passing ICAL.

12.5.3. Initial Calibration Blank (ICB):

12.5.3.1. Immediately following the ICV, analyze the ICB.

12.5.3.2. The ICB is deemed acceptable if it is ***≤ MDL/DL where the MDL/DL represents the current method detection limit for the target analyte.***

12.5.4. Continuing Calibration Verification (CCV)

12.5.4.1. Following establishment of a valid initial calibration, a continuing calibration verification (CCV) standard must be analyzed at the beginning of a sequence, bracketing every 10 samples throughout the sequence, and then at the end of the sequence.

12.5.4.2. The CCV is deemed acceptable if the %D is ≤ 10%. ***This criterion is applicable to all samples and projects including DOD work.***

12.5.4.2.1. If the %D is ≤ 10%, then the calibration is assumed to still be valid and sample analysis may continue.

12.5.4.2.2. If this criterion is not met, the CCV is deemed unacceptable. Reprepare and/or reanalyze the CCV one time. If the %D criterion remains unacceptable, effect corrective action, recalibrate the instrument, and reanalyze all samples analyzed since the last acceptable CCV.

12.5.5. Continuing Calibration Blank (CCB)

12.5.5.1. A continuing calibration blank (CCB) must be analyzed following each CCV throughout the analytical sequence.

12.5.5.2. ***The acceptance criterion for the CCBs is ≤ MDL/DL (when reporting to the MDL) where the MDL/DL represents the current method detection limit for the target analyte. If reporting to the RL or LOQ, the CCB is deemed acceptable if ND at or below ½ the RL or LOQ (DOD work).***

12.5.5.3. ***If the CCB fails (its result greater than the MDL/DL when reporting to the MDL or ≥ ½ RL/LOQ when reporting to the RL/LOQ) it should be immediately reanalyzed to confirm the detection.*** If it fails again, the analytical system is considered out of control, and the cause must be determined and corrected prior to the analysis of samples.

12.5.5.3.1. ***This would tend to indicate instrument contamination and may require that you change guard columns, sample tubing, or even the analytical column. Perform maintenance as needed to correct the contamination issue and***

then reanalyze all samples that are positive for hexavalent chromium.

12.6. ***Retention Time Window***

12.6.1. ***Prior to the analysis of samples, establish the retention time window for hexavalent chromium Cr(VI) as per the procedure outlined in SOP-T020.***

12.6.2. Daily retention time windows are based upon the retention time of the analyte in the CCV ± three times the mean standard deviation ***and are to be updated in the instrument method/data system after the analysis of the opening CCV (midpoint of the ICAL, if analyzed) and prior to further data processing.***

12.6.3. ***All subsequent standards in an analysis sequence must fall within the daily retention time window established by the first CCV. If not, identify the reason for the drift/shift, effect corrective action, and reanalyze any samples that are associated with/bracketed by those standards.***

12.6.4. ***Occasionally, sample matrix may create a shift in the retention time window for a sample that may also impact the following CCV. In this case, reanalyze the sample to confirm that matrix effects are the reason for the shift and not the instrument. In addition, post spiking the sample to confirm that the peak is in fact hexavalent chromium may be warranted in order to properly report the analyte in a sample.***

12.6.4.1. ***To post spike, estimate the concentration in the sample and then spike at a similar level. Reanalyze the post-spiked sample aliquot. If the peak is truly Cr(VI), it should essentially double in height and area. If the peak appears to be split at a value greater than 20% resolution, and/or two peaks are clearly present, then it has not been confirmed.***

12.6.5. ***Retention time windows shall be recalculated whenever a new column is installed.***

12.7. Method Blank (MB):

12.7.1. For aqueous samples, the MB consists of reagent water pH adjusted to 9.0–9.5 with buffer solution. For solid samples, the MB consists of washed sea sand.

12.7.2. The method blank is used to verify that the systems and processes are not contributing contamination to the preparation and/or analytical process. A method blank is prepared at a minimum rate of one for every 20 samples of the same matrix.

12.7.3. The concentration of hexavalent chromium in the method blank must be less than the reporting limit (RL) ***or ½ the LOQ if DOD.*** If the concentration of the target analyte exceeds its RL ***(½ LOQ),*** the source of contamination

must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.7.3.1. If hexavalent chromium is found in the MB, but not in the associated samples, report the sample and MB without qualification. ***Address the positive MB and the lack of impact on data quality in the narrative. Projects or programs may require correction action for a positive MB. This would consist of reanalysis of the associated samples.***

12.7.3.2. If hexavalent chromium is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination ***and reprepare and reanalyze the samples.***

12.7.3.2.1. ***Due to the short holding time for aqueous Cr(VI), reanalyzing the sample(s) within HT may not be feasible. If the result in the sample(s) is greater than 10x the MB level, chances are the impact on data quality will be minimal; however, reanalyze as soon as possible to confirm the concentration. Report the first set of data, flag the results with a "B", and narrate the event.***

12.7.4. Sample results will not be corrected for any values found in the associated method blank.

12.8. Laboratory Control Sample (LCS):

12.8.1. For aqueous samples, the LCS consists of the target analyte spiked into reagent water with buffer solution. For solid samples, the LCS consists of the target analyte spiked into washed sea sand. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control by measuring the percent recovery (%REC) of the spiked compound. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

12.8.1.1. One LCS is required for every batch of 20 samples per matrix or portion thereof.

12.8.1.2. When requested by client, to meet project DQOs, or if insufficient sample volume is received for an MS/MSD, a laboratory control sample duplicate (LCSD) is required.

12.8.1.3. The LCSD, when applicable, is handled identically to the LCS including frequency (every 20 samples). In addition to assessing accuracy, the LCS in combination with the LCSD can be used to assess the precision of the analytical process expressed as relative percent difference (RPD).

12.8.2. ***The acceptance criteria for Cr(VI) in the LCS is 80–120% recovery. If an LCSD is also analyzed, the %RPD is 20%. The criteria apply to routine and DOD project samples.***

12.8.2.1. ***The LCS (LCS/LCSD) must be within acceptance criteria for the batch to be valid. If not, the samples must be reanalyzed (reprepared and reanalyzed if solid samples) with an acceptable LCS with the following exceptions:***

12.8.2.1.1. ***If the LCS fails high and the associated samples are ND, the data may be reported with narration.***

12.8.2.1.2. ***If the samples are outside of holding time, and/or there is insufficient sample mass/volume to reprepare, report the original data, flag as needed, and address the impact to data quality in the case narrative.***

12.8.2.2. If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.

12.9. Matrix Spike / Matrix Spike Duplicate (MS/MSD):

12.9.1. The MS is the actual matrix spiked with a known concentration of the target analyte. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analyte. The measurement is expressed as percent recovery (%REC) of the spiked compound. The sample which is spiked for the MS is processed concurrently with the associated samples. The MSD is handled identically to the MS. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The precision is expressed as relative percent difference (RPD).

12.9.1.1. ***One MS/MSD pair is required for every batch of 20 samples per matrix or portion thereof.***

12.9.1.2. ***For solid samples processed by EPA 3060A, there will be two MS/MSD pairs: soluble and insoluble.***

12.9.1.3. ***The soluble MS/MSD data is loaded into LIMS and reported in the analytical report. The insoluble MS/MSD data is evaluated for recovery; however, the data is not reported due to a LIMS limitation. Instead, the raw data is maintained in the project file and is to be made available to the client upon request.***

12.9.2. ***The acceptance criteria for Cr(VI) in the aqueous MS/MSD is 70–130%, and the %RPD is 25%. The criteria apply to routine and DOD project samples.***

12.9.3. ***The acceptance criteria for Cr(VI) in the solid Soluble MS/MSD is 75–125% and the %RPD is 25%. The criteria apply to routine and DOD project samples.***

12.9.3.1. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance.

12.9.3.2. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

12.9.3.3. If the %REC or RPD of the MS/MSD and LCS are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and reanalyzed.

12.10. Additional information about internal quality control checks is provided in SOP-T020.

13. ▶CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 0.002 g (i.e., 2 mg), 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, ***remove from service and replace with a balance that meets criteria***.

13.2. Top Loading Balance

13.2.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.2.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, ***remove from service and replace with a balance that meets criteria***.

13.3. Pipetter

13.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.4. pH Meter Initial Calibration

13.4.1. Calibrate the pH meter daily prior to sample analysis at pH of 4.00, 7.00, and 10.00 using fresh buffer solutions and according to the instrument manufacturer's recommended procedures.

13.4.2. Verify the calibration with fresh second-source buffer standard. The second source standard shall not differ from its expected value by more than 0.05 pH units. If this criterion is not met, recheck calibration or effect corrective action.

13.4.2.1. The theoretical slope shall be within 90−105% for analysis to proceed. If this criterion is not met, determine the cause of the problem, effect corrective action, and recalibrate, if necessary.

13.4.3. ***Refer directly to SOP-M739 for additional information on the pH procedure.***

13.5. Ion Chromatograph

13.5.1. Prior to the analysis of samples, ***a valid blank + multi-point calibration curve shall be established. The ICAL must be verified by a passing ICV and ICB standard, prior to sample analysis.*** Samples may not be analyzed until a valid calibration curve is established.

14. ►PROCEDURE

14.1. Sample Preparation:

14.1.1. Solid Samples:

14.1.1.1. Follow the procedure as set forth in SOP-M224 (EPA 3060A), which involves alkaline digestion of hexavalent chromium in soils, sludges, sediments, and similar waste materials.

14.1.1.2. ***Check the conductivity of the digestate. If the conductance is below 4000 µS/cm, the sample may go directly to analysis. If the conductivity is greater than 4000 µS/cm, pretreat as follows:***

14.1.1.2.1. To reduce the conductivity prior to analysis, the filtrates should be passed through a series of pretreatment cartridges. For this pretreatment, three cartridges are attached in series in the following order: Ba, Ag, and H.

14.1.1.2.2. Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to ensure all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

14.1.1.2.3. Pretreated QC samples (MB and LCS) are used to verify that no background interference or bias is contributed by the pretreatment. If a response is observed in the pretreated LCS, triple or quadruple the volume of reagent water used for the rinse and repeat until a blank measures no more than ½ the RL. If this additional rinsing procedure is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment on any additional sample or QC aliquots.

14.1.1.2.4. Filter 1–2 mL of the sample through the series of rinsed, stacked cartridges as an initial sample rinse at a flow rate of one drop every 3 to 4 seconds (approximately 1.0 mL/min or less). This flow rate is critical to the pretreatment and must be carefully followed. Discard this fraction and begin collecting the pretreated sample aliquot.

14.1.1.2.5. When sufficient volume has been collected (5–10 mL), measure the conductance of the pretreated sample aliquot, being certain the conductivity meter's probe has been thoroughly rinsed and excess water has been shaken from the tip.

14.1.1.2.6. If the conductance is below 4000 µS/cm, the sample is ready for analysis. If the conductance is still above 4000 µS/cm, the flow rate through the pretreatment cartridge is likely too fast, and the pretreatment should be repeated with new cartridges. In some instances, double pretreatment cartridges may need to be applied.

14.1.1.3. Following digestion by EPA 3060A and optional cartridge pretreatment, the filtrates are ready for analysis by EPA 7199 and will follow the procedures noted below for aqueous samples.

14.1.2. Aqueous Samples:

14.1.2.1. Allow samples to reach ambient temperature prior to filtration and pH adjustment.

14.1.2.1.1. All samples and QC (MB, LCS, LCSD, Duplicates, MS, and MSD, as applicable) must be filtered and have the pH adjusted prior to analysis.

14.1.2.2. ***QC Samples (LCS, MS, and MSD) must be spiked prior to filtration and pH adjustment***

14.1.2.2.1. ***For the aqueous LCS and MS/MSD, add 100 µL buffer to 10 mL of the sample and spike with 50 µL of the second-source 10-ppm working standard; filter and transfer approximately 4 mL to an autosampler vial and analyze.***

14.1.2.2.2. ***For the low-level aqueous MS/MSD, add 100 µL buffer to 10 mL of the sample and spike with 10 µL of the second-source 10-ppm working standard solution; filter and transfer 4 mL to an autosampler vial.***

14.1.2.3. To filter QC and field samples: using a 10-mL disposable plastic syringe, draw approximately ***8–10*** mL of sample into the syringe

by pulling back on the syringe plunger. Once the syringe is full, attach a 0.45-µm filter disk to the syringe tip. Slowly push down on the plunger until the sample begins to pass through the filter disk. Dispose of the first 0.5 mL of sample filtrate. Continue pushing down on the plunger until the sample has passed through the filter disk and collect the filtrate in a 120-mL plastic specimen container ***(if keeping additional filtrate for reanalysis) or directly into the autosampler vial.*** Do not use excessive force as the filter disk may rupture. Use a new syringe and filter disk for each sample.

14.1.2.4. Once filtered, adjust the pH of each field sample to between 9.0 and 9.5 by transferring 4 mL of filtrate into an autosampler vial and adding 40 µL of buffer solution (Section 10.1.***10***.) Use narrow-range pH paper to check the pH of the filtrate before and after adjustment by transferring a drop of filtrate onto the pH paper a capillary tube or disposable pipette. Record the initial and final pH values in the Sample Preparation Logbook.

14.1.2.4.1. If salts are formed as a result of pH adjustment, the samples must be filtered again to remove solids.

14.1.2.5. Once the filtrate has been sufficiently buffered, it is ready for analysis. Cap the vial and place on the autosampler.

14.2. ***Sample Analysis***

14.2.1. ***Daily Retention Time Window***

14.2.1.1. ***The method retention time window must be updated prior to sample or standard processing.***

14.2.1.1.1. ***Following the analysis of the initial CCV, or using the midpoint calibration standard if a new ICAL was performed, update the retention time in the instrument method. See section 12.5. for additional information.***

14.2.2. ***ICAL or Opening CCV***

14.2.2.1. ***If the instrument requires calibration, proceed with the analysis of the calibration blank and then the sequential standards. Follow with the ICV/ICB. The ICAL must be valid prior to initiating sample and QC analyses.***

14.2.2.2. ***If the ICAL is not needed, the sequence will start with the analysis of a CCV, followed by a CCB. If these meet defined acceptance criteria, sample and QC analysis may proceed. A CCV/CCB pair must be analyzed every 10 samples (every 10 injections for certain programs) and at the end of the analytical sequence.***

14.2.3. Continuing Calibration (CCV) Analysis

14.2.3.1. The ICAL is verified through the analysis of continuing calibration verification standards (CCVs). The concentration of the CCV is at or near the midpoint of the curve ***(50 ppb)***. Opening, bracketing, and closing CCV's are required to be analyzed.

14.2.3.2. The acceptance criterion for the CCV is a %D ≤ 10%.

14.2.3.2.1. If the CCV meets this criterion, sample analysis may continue. If the CCV fails, it should be reanalyzed, or reprepared and reanalyzed. If it fails again, the analytical system is considered out of control, perform corrective action and recalibrate. Samples may not be analyzed until a valid calibration curve is established.

14.2.3.2.2. If the ***bracketing/ending*** CCV does not meet acceptance criterion, then all sample data obtained since the last acceptable CCV must be invalidated and the samples reanalyzed.

14.2.3.2.2.1. ***If the closing CCV is high and the associated samples are ND, reanalyze the CCV to confirm. If still high or within criteria, report the ND data with narration. If low, reanalyze all samples with a passing CCV/ICAL. If there is insufficient sample volume remaining for reanalysis, then the data must be qualified and the QC issue addressed in the report narrative.***

14.2.4. Continuing Calibration Blanks:

14.2.4.1. Satisfactory instrument baseline is continually assured through the analysis of continuing calibration blanks (CCBs). CCBs are reagent water with buffer solution added, without any preparatory steps. Opening, bracketing, and closing CCBs are required to be analyzed.

14.2.4.1.1. Prepare CCBs by diluting 1.0 mL of buffer to a final volume of 100 mL with reagent water.

14.2.4.1.2. The acceptance criterion for CCBs is 0 ± MDL where MDL represents the current MDL value. If the CCB fails, it should be reanalyzed. If it fails again, the analytical system is considered out of control and the cause must be determined and corrected prior to the continued analysis of samples.

14.2.4.1.3. If the ending CCB still does not meet the acceptance criterion, then all sample data obtained since the last acceptable CCB must be invalidated and the samples reanalyzed with a passing CCB. ***However, as with the MB, if the CCB is positive, the CCV is within criteria, and the associated samples are ND, the data may be reported with narration***.

14.3. Analysis ***Sequence***

14.3.1. Autosampler vials are loaded onto the sample tray and analytic processing commenced. If an initial calibration has not been established, load the calibration standards and ICV/ICB prior to the analysis of client and QC samples.

14.3.2. In general, the following will apply to all sample sequences:

14.3.2.1. An instrument blank will be analyzed first, and it must be clean.

14.3.2.2. A calibration blank will be the first 'calibration standard' analyzed, and it will be included in the calibration curve.

14.3.2.3. The method blank will be analyzed immediately following the ICV/ICB or opening CCV/CCB.

14.3.2.4. An opening CCV/CCB pair will be analyzed along with bracketing, every 10 samples, and closing CCV/CCBs as per the sequence noted below, and corrective action performed if needed.

14.3.2.5. An LCS or LCS/LCSD and MS/MSD pair will be analyzed for every batch of 20 samples.

14.3.2.6. A batch will consist of a method blank, LCS or LCSLCSD pair, MS/MSD pair, and up to 20 field samples.

14.3.3. Run samples in the following or other logical order:

Instrument blank
*Cal Blank (for 7199)
*Cal Standard 1
*Cal Standard 2
*Cal Standard 3
*Cal Standard 4
*Cal Standard 5
*Cal Standard 6
*Cal Standard 7
*ICV
*ICB
CCV (Opening)
CCB
Method Blank
LCS

LCSD, when applicable
10 field samples
MS
MSD
CCV
CCB
10 field samples
CCV
CCB

* The initial calibration and initial calibration verification and blank samples are only analyzed when the instrument needs to be calibrated. They are included in the daily analytical sequence table to assist the data processing.

14.4. Set up the ion chromatograph in preparation for the analytical sequence.

14.5. Edit the sequence in the data system. After all correct sample, ***standard, and consumable traceability information is entered,*** save the sequence.

14.6. ***After saving the sequence, print out a copy, stamp with the controlled stamp, three hole punch, and place in the run log binder.***

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window of the target analyte ***by updating the instrument method with the retention time of the opening CCV, or the midpoint of the ICAL if a new ICAL was performed.***

14.8.1.1. Tentative identification of an analyte occurs when a peak from a sample or sample extract falls within the daily retention time window.

14.8.1.2. Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and effect appropriate corrective action.

14.8.2. Quantitation of the target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample or sample extract and the calibration standards.

14.8.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2. Determine the concentration based on the initial calibration curve.

14.8.2.3. If the instrument response exceeds the calibration range, dilute the sample or sample extract and reanalyze.

15. CALCULATIONS

15.1. The percent difference of the analyte is calculated as follows:

$$\%D = \frac{|C_m - C_t|}{C_t} X\,100$$

where: %D = percent difference (or percent drift) of the target analyte.
C_m = measured concentration of the target analyte (µg/L).
C_t = true concentration of the target analyte (µg/L).

15.2. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) x\,100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

15.3. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) x\,100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in the sample used.
C_{added} = concentration of target analyte added.

15.4. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} x\,100$$

where: RPD = relative percent difference between C_1 and C_2.
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.5. The concentration of the injected sample is read directly from the display and is calculated as follows:

$$C_f\ (\mu g/L) = C_d \times DF$$

where: C_f = final concentration in sample (µg/L).
C_d = concentration obtained directly from the display (µg/L).
DF = dilution factor.

15.6. Sample concentration for solid samples is calculated as follows:

$$C_s\ (\mu g/kg) = \frac{(C_d \times DF \times V_{ex})}{W_s}$$

where: C_s = concentration of the target analyte in the solid sample (µg/kg).
C_d = concentration obtained directly from the display (µg/L).
DF = dilution factor.
V_{ex} = extract volume in mL.
W_s = weight of solid sample extracted in g.

15.7. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for solid samples.

15.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. ►METHOD PERFORMANCE

16.1. A demonstration of analytical capability ***(MDL study, MDL verification, and IDOC for the method and analyst)*** shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix, or test method.

16.2. Proficiency test sample results shall be used to evaluate the ability to produce accurate results. ***PT samples must be managed exactly as a field sample.***

17. ►POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses, lab coats and gloves are required to be worn when handling chemicals and samples.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves as well as a full-length laboratory apron.

17.3.3. Face shield and or safety glasses.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ***Refer to Section 12 for quality control requirements and corrective actions.***

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for soil and solid waste samples.

18.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ►CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, Quality Control Manager ***or designee***, Group Leader, and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ▶CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS: Corrective action ***must*** be taken for an LCS failure. Because they denote whether the analytical system is operating within control, LCS recoveries ***must be*** within acceptance criteria, ***with the exceptions noted in section 12.3.1.*** If the recoveries fail, the group leader confirms the unacceptable result ***and initiates corrective action.***

20.1.2. MS/MSD: ***Corrective action is not taken for MS/MSD failures if the LCS is within criteria.*** At that point, the MS/MSD failure is attributed to matrix effects—either reducing or oxidizing—and the insoluble spike should be assessed. (***In addition, reference to initial pH and REDOX potential analyses, if performed, and their evaluation against a Pourbaix***

diagram should be made in order to fully evaluate the presence and state of hexavalent chromium in the associated field samples.)

20.1.2.1. If the LCS and MS/MSD are all outside criteria then the samples require repreparation/reanalysis.

20.1.2.2. If there is insufficient sample volume for reanalysis, or repreparation and analysis, the QC issue should be addressed in the report narrative.

21. ▶WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste. ***These containers shall be emptied into appropriate satellite waste containers or other appropriate waste receptacles, daily.***

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. ▶REFERENCES

22.1. US EPA, Method 7199, Determination of Hexavalent Chromium In Drinking Water, Ground Water and Industrial Wastewater Effluents by Ion Chromatography, Revision 0, December 1996.

22.2. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

22.3. ***Department of Defense Quality Systems Manual for Environmental Laboratories, Version 5.0, July 2013.***

23. APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Not Applicable.

24. ►MODIFICATIONS

24.1. The following modifications to method EPA 7199 are noted.

Calscience SOP M737 Section	Reference Document EPA 7199 Section	Summary of Modification
10.2	5.8	Dilution water not prepared; direct addition of buffer to samples and standards is done instead.
14.4	7.4	Samples not injected twice.

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
1.2	Minor typos corrected throughout. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample storage. Section 13: Update equipment calibration. Section 14: Update procedure. Section 18: Add data assessment section. Section 24: Add modifications section. Section 25: Add revision history section.	K. Burney	06/29/12

Revision	Description	Author	Effective Date
1.3	Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample container and storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 20: Update contingencies. Section 23: Add appendix. Section 24: Update Modifications. Section 25: Update Revision History.	K. Burney	01/20/14
1.4	Entire document: Update company name. Section 3: Change EQLs to RLs. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 19 and 20: Update responsibilities.	L. Hunt	03/30/15
2.0	Entire SOP updated to include additional information and clarification as to procedures.	L. Scharpenberg	06/01/2015

Title : **EPA METHOD 7470A, MERCURY IN LIQUID WASTE (COLD-VAPOR TECHNIQUE)**

Document No. : SOP-M619
Revision No. : 3.1
Supersedes : 3.0

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PROPRIETARY INFORMATION STATEMENT

Revision 3.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/31/15
MANAGEMENT **DATE**

_____ 03.31.15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature
	03/22/16		

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique).

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous wastes, ground waters, and mobility-procedure extracts.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs) for this method*** for this method are as follows:

	Aqueous
Mercury	0.00050 mg/L
Low Level Mercury	0.000050 mg/L

3.2. The ***RLs*** will be proportionally higher for samples which require dilution.

3.3. The ***RLs*** will be proportionally lower or higher for samples which require mobility extraction.

3.4. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

3.5. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. EPA Method 7470A is a cold-vapor atomic absorption procedure for determining the concentration of mercury (Hg). All samples must be subjected to an appropriate dissolution step prior to analysis.

4.1.1. The method can also be used for analyzing certain solid and sludge-type wastes; however, EPA Method 7471B is usually the method of choice for these waste types.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of atomic absorption spectrometer, skilled in the interpretation of atomic absorption spectra, and knowledgeable in the correction of interferences described in this method.

5. METHOD SUMMARY

5.1. Cold-vapor atomic absorption (CVAA) technique is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption

spectrometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.2. Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.

5.2.1. Aqueous samples are digested with acids.

5.2.2. Aqueous and solid samples for waste characteristic analysis are prepared via the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are digested with acids.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Terms Specific to Mercury Analysis

6.26.1. Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

6.26.2. Dissolved Mercury: The concentration of mercury determined in a filtered sample following digestion with acids.

6.26.3. Lower Limit of Quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.

6.26.4. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The standard addition

technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.26.5. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.26.6. Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration. For atomic absorption, the concentration of metal, in mg/L, that produces a transmission of 1% is commonly employed to determine sensitivity.

6.26.7. Total Mercury: The concentration of mercury determined in an unfiltered sample following digestion with acids.

7. INTERFERENCES

7.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

7.2. Copper may interfere; however, copper concentrations as high as 10 mg/L have no effect on the recovery of mercury from spiked samples.

7.3. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

7.3.1. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL).

7.4. Certain volatile organic materials that absorb at the wavelength of 253.7 nm may also cause interference.

7.4.1. A preliminary run without reagents may be used to determine whether this type of interference is present.

8. ►SAFETY

8.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Atomic Absorption Spectrometer: PerkinElmer Flow Injection Mercury System (FIMS) 400 or equivalent configured with the following components:

9.1.1. Computer-controlled atomic absorption spectrometer, single-beam optical system, with 254-nm maximum sensitivity.

9.1.2. Solar-blind detector.

9.1.3. Mercury lamp, high intensity, low pressure.

9.1.4. Absorption cell, 240-mm × 7-mm OD × 4-mm ID, quartz.

9.1.5. Two peristaltic pumps, 20−120 rpm variable speed, computer controlled.

9.1.6. Sample loop, 200 µL.

9.1.7. Autosampler, PerkinElmer AS-90 Autosampler or equivalent.

9.1.8. Autosampler vessels, 16-mm OD (15-mL capacity), translucent polypropylene, disposable.

9.1.9. Autosampler vessels, 30-mm OD (50-mL capacity), with screw caps, translucent polypropylene, disposable.

9.2. Instrument Software

9.2.1. Requires a PC-based data system or equivalent.

9.2.2. PerkinElmer WinLab 32 for AA or equivalent, capable of automatic baseline offset correction.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. Carrier Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.5. Graduated cylinders, 100-mL or other capacity, glass, Class A.

9.6. Volumetric flask, 100-mL or other capacity, glass, Class A.

9.7. Pipetters, 100–1000 µL, 0.5–5.0 mL, and 1–10 mL, calibrated, adjustable, with disposable tip.

9.8. Refer to Appendix A for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Hydrochloric acid, HCl, 32–35% or 34–37% (v/v), concentrated, clear colorless liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.3. Hydrochloric acid, HCl, 3% (v/v).

10.1.3.1. Prepare the 3% HCl solution by slowly adding 60 mL of concentrated HCl to 500 mL of reagent water and dilute to 2 L with additional reagent water.

10.1.3.2. The 3% HCl solution is used as the carrier solution.

10.1.3.3. It is also used as a rinse blank to flush the system between standards and samples to minimize interferences.

10.1.4. Nitric acid, HNO_3, 67–70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.5. Nitric acid, HNO_3, 1:1 (v/v).

10.1.5.1. Prepare the 1:1 HNO_3 solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and dilute to 1 L with additional reagent water.

10.1.6. Stannous chloride, $SnCl_2$, dihydrate, white crystalline powder, reagent grade or equivalent.

10.1.7. Stannous chloride solution, $SnCl_2 \cdot 2H_2O$/HCl.

10.1.7.1. Prepare the stannous chloride solution by adding 11 g of $SnCl_2 \cdot 2H_2O$ to 1 L of 3% HCl solution.

10.1.7.2. The stannous chloride solution is used as the reducing agent.

10.1.8. Refer to Appendix A for additional reagents.

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions, 99.990–99.999% source purity, each in sealed polyethylene bottles, containing 1000/100 ppm of mercury are used to prepare calibration and check standards.

10.2.1.2. Prepare each mercury working standard solution by diluting the appropriate volume of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.1.3. The working standards are prepared as follows:

	Initial		Final	
Analyte	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	1000	0.2	2.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

	Initial		Final	
Analyte	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	100	1.0	1.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

10.2.1.4. The working standard solutions must be replaced after one month or sooner if comparison with check standards indicates a problem.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Measure 0.5 mL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

10.2.2.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

10.2.2.3. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

10.2.2.4. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.2.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

10.2.2.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.2.7. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.2.9. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 10.0-ppb initial calibration standard.

10.2.2.10. Dilute the appropriate volumes of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain other initial calibration standards.

10.2.2.11. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.12. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	10.0	0.05	20.0
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.13. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

10.2.2.14. The initial calibration standard solutions must be prepared fresh daily.

10.2.3. Calibration Blank (CB)

10.2.3.1. Designate a minimum of five clean digestion tubes for calibration blank preparation.

10.2.3.2. Measure 50 mL of reagent water into each clean digestion tube.

10.2.3.3. Slowly add 2.5 mL of concentrated H_2SO_4 to each digestion tube and mix.

10.2.3.4. Slowly add 1.25 mL of concentrated HNO_3 to each digestion tube and mix.

10.2.3.5. Add 7.5 mL of the 5% $KMnO_4$ solution to each digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.3.6. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to each digestion tube.

10.2.3.7. Place each digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.3.8. Remove the digestion tubes from the block digester and allow the digested reagent water to cool.

10.2.3.9. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested reagent water to reduce excess permanganate.

10.2.3.10. The CB is used to establish the zero point of the calibration curve or to dilute standards and samples.

10.2.3.11. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.4. Method Blank (MB)

10.2.4.1. Process the MBs using the appropriate sample preparation procedure.

10.2.4.2. The MB is used to identify possible contamination resulting from either the reagents or the equipment used during sample processing.

10.2.5. Initial Calibration Verification (ICV) Solution

10.2.5.1. Measure 0.5 mL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

10.2.5.2. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

10.2.5.3. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

10.2.5.4. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

10.2.5.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

10.2.5.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

10.2.5.7. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.5.9. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 5.0-ppb ICV solution.

10.2.5.10. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.11. The ICV solution must be prepared fresh daily.

10.2.6. Continuing Calibration Verification (CCV) Solution

10.2.6.1. Dilute 4.0 mL of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain the 2.0-ppb CCV solution.

10.2.6.2. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.6.3. The CCV solution must be prepared fresh daily.

10.2.7. Refer to Appendix A for additional standards.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. Aqueous samples for dissolved mercury determination shall be field filtered through a 0.45-µm filter within 15 minutes of sample collection and preserved with 1:1 HNO_3 solution to pH < 2.

11.1.1.1. If the samples are field filtered but not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion and analysis.

11.1.2. Aqueous samples for total mercury determination shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.1.2.1. If the samples are not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion and analysis.

11.2. Mobility-procedure extracts should be collected in 3-oz pre-cleaned polypropylene digestion tubes with polypropylene lids, or 250-mL pre-cleaned HDPE containers with Teflon-lined closures.

11.2.1. Mobility-procedure extracts shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2.2. If precipitate is observed upon the addition of 1:1 HNO_3 solution to a small aliquot of the mobility-procedure extract, do not acid preserve the mobility-procedure extract. Digest the mobility-procedure extract within 24 hours.

11.3. Aqueous samples shall be maintained in a chilled state ***(0–6°C)*** post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Upon receipt, the samples are stored in a 0–6°C cooler.

11.4.1. Unfiltered aqueous samples for dissolved mercury determination must be filtered as soon as possible and preserved with 1:1 HNO_3 solution to pH < 2 immediately after filtration.

11.4.1.1. The samples may then be digested and analyzed within 28 days of sample collection.

11.4.2. Filtered aqueous samples with acid preservation (pH < 2) for dissolved mercury determination must be digested and analyzed within 28 days of sample collection.

11.4.3. Filtered aqueous samples without acid preservation (pH ≥ 2) for dissolved mercury determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 28 days of sample collection.

11.4.4. Aqueous samples with acid preservation (pH < 2) for total mercury determination must be digested and analyzed within 28 days of sample collection.

11.4.5. Aqueous samples without acid preservation (pH ≥ 2) for total mercury determination must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 28 days of sample collection.

11.4.6. Mobility-procedure extracts with acid preservation (pH < 2) must be digested and analyzed within 28 days post mobility extraction.

11.4.6.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.4.7. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be preserved with 1:1 HNO_3 solution to pH < 2 immediately after mobility extraction.

11.4.7.1. The mobility-procedure extracts may then be digested and analyzed within 28 days post mobility extraction.

11.4.7.2. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established daily prior to the processing of samples.

12.1.1.1. The calibration curve is established with one calibration blank and five or six calibration standards.

12.1.2. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression of each analyte is ≥ 0.995.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibrate.

12.3. Initial Calibration Blank (ICB)

12.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Blank (CCB)

12.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB.

12.6. Contract Required Quantitation Limit (CRQL) Check

12.6.1. A CRQL check standard is analyzed immediately following the ICV/ICB analyses.

12.6.1.1. The concentration of each analyte in the CRQL check solution shall be at the lowest calibration level.

12.6.2. The linearity of the calibration curve is deemed verified if the recovery of each analyte is within 70−130%.

12.6.3. CRQL check is performed per client request or project specific DQOs to verify the linearity of the calibration curve.

12.7. Lower Limit of Quantitation (LLOQ) Check

12.7.1. An LLOQ check sample is analyzed immediately following the ICV/ICB analyses.

12.7.1.1. The concentration of each analyte in the LLOQ check sample is at the established laboratory reporting limit.

12.7.1.2. The LLOQ check sample shall be carried through the entire preparation and analytical procedure.

12.7.2. The lower limit of quantitation is deemed verified if each analyte is detected at within ± 30% of its expected value.

12.7.3. LLOQ check is performed per client request or project specific DQOs to demonstrate the desired detection capability.

12.8. ►Event Based Quality Control (LCSs and MBs)

12.8.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample ***(LCS)*** and, ***if required***, laboratory control sample duplicate (LCSD) and a method blank (MB).

12.8.1.1. ***An LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.***

12.8.2. The acceptance criteria for LCS elements are as follows:

12.8.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS element are based upon the historical average recovery ± 3S that is updated at least annually.

12.8.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS element are 80% and 120%, respectively. ***When an LCSD is prepared and analyzed,*** the RPD is ≤ 20%.

12.8.2.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.8.2.2. All LCS elements must be within acceptance limits. If the LCS elements are not acceptable, determine the cause of the problem and effect corrective action.

12.8.3. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific data quality objective (DQO). In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.8.3.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.8.3.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.9. Matrix Based Quality Control (MS/MSDs and PDSs)

12.9.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.9.2. The acceptance criteria for MS/MSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.9.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.9.2.1.2. ►The acceptance limits derived from historical data should not be wider than ± ***25%*** for accuracy and 20% for precision.

12.9.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision

requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.9.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.9.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

12.10. If the %REC or RPD of the MS/MSD and LCS are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.11. Dilution Test

12.11.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.11.2. If this criterion is not met, then a chemical or physical interference effect should be suspected. Perform post digestion spike addition.

12.11.3. Dilution test is performed per client request or project specific DQOs.

12.12. Post Digestion Spike Addition

12.12.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10−100 times the RL.

12.12.2. The acceptance criteria for PDS elements are as follows:

12.12.2.1. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

12.12.2.2. If the %REC of a PDS element is not within the established acceptance limits, then matrix effects should be suspected. Perform MSA on all samples in the same preparation batch.

12.12.3. Matrix effects are confirmed if the %REC values of both the MS/MSD and the PDS are unacceptable.

12.12.4. Post digestion spike addition is performed per client request or project specific DQOs.

12.13. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Pipetter

13.1.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.2. Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.

13.2.2.1. Per client request or project specific DQOs, a CRQL check standard must be analyzed immediately following the ICV/ICB analyses to verify the linearity of the calibration curve. The acceptance criteria for the CRQL are listed in Section 12.6.

13.2.2.2. Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the ICV/ICB analyses to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.7.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. ▶PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 15 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. Use the following CVAA operating conditions as guidance.

Description	Operating Condition
Carrier gas flow	40~70 mL/min
Pump #1 speed	100 rpm
Pump #2 speed	120 rpm
Carrier solution / sample diluent (3.0% HCl)	9~11 mL/min
Reductant (1.1% $SnCl_2$ in 3.0% HCl)	5~7 mL/min
Reaction coil	110-mm × 1.0-mm ID
Wavelength	253.7 nm
Number of replicates	2

14.1.1.2. Autosampler is set to inject 200 µL of field or QC sample digestate.

14.1.2. Place the inlet of the blue/yellow carrier solution pump tube in the hydrochloric acid reservoir. Place the inlet of the red/red reductant pump tube in the stannous chloride reservoir. Position the sampling probe in the reagent water reservoir.

14.1.3. Check the carrier solution and reductant flow rates. The reductant flow rate should be approximately one half of the carrier solution flow rate.

14.1.3.1. Check the flow rate by placing the inlet of the tube in a graduated cylinder filled with reagent water, and then measure the volume decrease after one minute.

14.1.3.2. If the flow rate is not within the appropriate range, adjust the pump pressure for the tube until the flow rate is within range.

14.1.4. Program the system to average two integrations on each blank, standard, and sample. Report the average.

14.1.4.1. If the %RSD for an analyte in a standard is > 10%, document the unacceptable result and reanalyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.4.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, document the unacceptable result and reanalyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish a calibration curve to cover the appropriate concentration range (see Section 13.2.).

14.3. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.

14.3.1. If a failed CCV/CCB is the first of the day, effect corrective action and reanalyze all samples since the last acceptable ICV/ICB.

14.3.2. If a failed CCV/CCB is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.4. Following preparatory procedures specified in Appendix A, the digestates for the QC and actual environmental samples are received in digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels are then loaded onto the system sample tray.

14.5. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) CRQL or LLOQ Check (per client request or project specific DQOs)
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD), ***when required***
9) Samples (up to 10 per batch, including QC check samples and MBs)
10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Dilution Test Sample (per client request or project specific DQOs)
15) Post Digestion Spike (PDS) (per client request or project specific DQOs)
16) Samples (up to 10 per batch, including QC check samples and MBs)
17) Ending CCV
18) Ending CCB

14.5.1. Item 1: The CB is an aliquot of reagent water digestate used to establish the zero point of the initial calibration curve.

14.5.2. Item 2: The initial calibration standards are used to establish the initial calibration curve.

14.5.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial multi-point calibration. An acceptable ICV is required daily after initial calibration.

14.5.4. Item 4: The ICB is an aliquot of reagent water digestate used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.5.5. Item 5: The CRQL check standard is used to verify the linearity of the calibration curve. The LLOQ check sample is used to verify the lower limit of quantitation. Per client request or project specific DQOs, an acceptable CRQL or LLOQ check is required immediately following ICV and ICB.

14.5.6. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.5.6.1. For aqueous samples, the MB consists of clean reagent water. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.5.6.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.6.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water digestate must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.5.7. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.5.7.1. For aqueous samples, the LCS consists of the specified element spiked into clean reagent water. For mobility-procedure extracts, the LCS consists of the specified element spiked into the mobility-procedure extract designated as LCS.

14.5.7.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.8. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.9. Items 9 and 16: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates with concentrations exceeding the calibration range should be sufficiently diluted. Dilution of digestates will result in increased reporting limits.

14.5.9.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.5.10. Items 10 and 17: A CCV is a standard used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.5.11. Items 11 and 18: A CCB is an aliquot of reagent water digestate used to monitor contamination. An acceptable CCB is required immediately following CCV.

14.5.12. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the

MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.5.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.13. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.14. Item 14: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.5.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.5.14.2. To comply with client request or project specific DQOs, one dilution test sample is required daily for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.15. Item 15: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentration of specific target analyte post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.5.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.5.16. Rinse blanks consisting of 3% HCl solution may be added elsewhere in the sequence to rinse the analytical system.

14.6. Ensure that sufficient amounts of 3% HCl solution and stannous chloride solution are present in the 3% HCl and stannous chloride reservoirs, respectively, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.7. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7.1. Record the reagent and standard identification numbers on the sequence table printout.

14.8. Initiate the sequence.

14.9. Data Interpretation

14.9.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between absorbances in the sample digestate and the calibration standards.

14.9.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the absorbance of an element can be determined.

14.9.1.2. Determine the concentration based on the initial calibration curve.

14.9.1.2.1. The data system is programmed to perform the calculation of concentration via the Beer-Lambert Law.

14.9.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

14.10. Method of Standard Additions (MSA)

14.10.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.10.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition.

14.10.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the digested reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.8. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If

a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.10.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix B. A linear regression program may be used to obtain the intercept concentration.

14.10.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.10.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.10.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.10.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{A_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the absorbances for the target analyte.
A_{ave} = mean of the absorbances for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.7. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_x \times V_x \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
V_{MP} = volume of mobility-procedure extract digested in mL. Unless specified otherwise, V_{MP} = 10.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.9. Refer to the mobility extraction method(s) for additional calculations.

15.10. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ►POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD elements must be within acceptance limits.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.2. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific DQO. In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of the target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.3. The acceptance criteria for MS/MSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

18.4.1. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are

confirmed. Perform MSA (see Section 14.10.) on all samples in the same preparation batch.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ▶CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, ***Quality Control Director***, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the ***group leader*** confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Mercury in Liquid Waste (Manual Cold-Vapor Technique), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7470A, USEPA, Revision 1, September 1994.

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/7470a.pdf

22.2. Flame Atomic Absorption Spectrophotometry, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

22.3. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. Inorganic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ►Appendix A: Sample Preparation and Digestion Procedures.

23.2. Appendix B: Standard Addition Plot (Example).

23.3. Appendix C: Additional Quality Control Criteria for Department of Defense Project.

23.4. ***►Appendix D: EPA Method 7470A Procedure Outline.***

23.5. Appendix E: Multiple Calibration Standard Digestion.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 7470A are noted.

24.1.1. Reagents and Standards

24.1.1.1. Standard preparations are modified.

24.2. The following modifications from EPA Method 7000B are noted.

24.2.1. Quality Control

24.2.1.1. The criteria of method blank and post digestion spike addition are modified.

25. ►REVISION HISTORY

Description	Author	Effective Date
SOP revision.	X. Xu	11/15/10
SOP revision.	L. Lem	11/12/12
Added Appendix E	X. Xu, L. Lem	08/12/13
Entire Document: Update company name. Section 3: Change EQLs to RLs. Section 6: Update definitions. Sections 8 and 17 and Appendix A: Add SDS. Section 11: Update temperature. Sections 12, 14, and 18 and Appendices A and C: Update LCSD requirement. Sections 20 and 21: Update responsibilities. Delete (former) Appendix D: Additional Quality Control Criteria for BP Project. Appendix D: Add procedure outline.	L. Hunt	03/30/2015

Appendix A

SAMPLE PREPARATION AND DIGESTION PROCEDURES

Eurofins Calscience, Inc.

METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique) – Sample Preparation and Digestion Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipment and apparatus required to execute the procedure.

3. METHOD SUMMARY

3.1. EPA Method 7470A provides digestion and cold-vapor atomic absorption conditions for the analysis of mercury in liquid waste.

4. INTERFERENCES

4.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.2. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

5. ►SAFETY

5.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

5.2. All sample preparation activities must be performed in a fume hood vented to the exterior of the laboratory.

5.2.1. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

5.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the digestion.

5.4. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform digestions alone. Another chemist should be present during any digestion process.

5.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Digestion tubes (vials), 4-oz (120-mL), 90-mm × 43-mm ID, graduated, snap closure, with hinged lids, polypropylene, disposable, Capitol Vial P/N 04HPLS or equivalent.

6.2. pH indicator paper, narrow range. pH range should include the desired pH.

6.3. Watch glass, ribbed or equivalent, glass, appropriate diameter to cover vial.

6.4. Pipetters, 100–1000 µL, 0.5–5.0 mL, and 1–10 mL, calibrated, adjustable, with disposable tip.

6.5. Dispensers, 1–10 mL, 2.5–25 mL, and 5–50 mL, calibrated, adjustable.

6.6. Thermometer, calibrated, capable of accurately measuring at 95°C.

6.7. Block digester, equipped with water bath, capable of maintaining 95°C.

6.8. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

6.9. Syringe filtration apparatus:

6.9.1. Syringe, 10 mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

6.9.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing, disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free, nano-pure.

7.1.2. Nitric acid, HNO_3, 67–70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

7.1.3. Nitric acid, HNO_3, 1:1 (v/v).

7.1.3.1. Prepare the 1:1 HNO_3 solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and dilute to 1 L with additional reagent water.

7.1.4. Sulfuric acid, H_2SO_4, 93–98% (v/v), concentrated, clear colorless to yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

7.1.5. Sodium chloride, NaCl, fine white crystals, reagent grade or equivalent.

7.1.6. Hydroxylamine hydrochloride, $H_3NO{\cdot}HCl$, fine white crystalline powder, reagent grade or equivalent.

7.1.7. Sodium chloride-hydroxylamine hydrochloride solution, $NaCl\text{-}H_3NO{\cdot}HCl$.

7.1.7.1. Prepare the sodium chloride-hydroxylamine hydrochloride solution by dissolving 2400 g of NaCl and 2400 g of $H_3NO{\cdot}HCl$ in reagent water and dilute to 20 L with additional reagent water.

7.1.8. Potassium permanganate, $KMnO_4$, dark purple to green crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.9. Potassium permanganate, $KMnO_4$, 5% (w/v).

7.1.9.1. Prepare the 5% $KMnO_4$ solution by dissolving 1000 g of $KMnO_4$ in 20 L of reagent water.

7.1.10. Potassium persulfate, $K_2S_2O_8$, fine white crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.11. Potassium persulfate, $K_2S_2O_8$, 5% (w/v).

7.1.11.1. Prepare the 5% $K_2S_2O_8$ solution by dissolving 500 g of $K_2S_2O_8$ in 10 L of reagent water.

7.1.12. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. Standards

7.2.1. Stock Standard Solution

7.2.1.1. Pre-certified stock standard solution, 99.990–99.999% source purity, in sealed polyethylene bottle, containing 1000 ppm of mercury is used to prepare check standards.

7.2.1.2. Prepare the 2.0-ppm mercury working standard solution by diluting 0.2 mL of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

7.2.2. Spike Standard Solution

7.2.2.1. Use the 2.0-ppm mercury working standard solution as the spike standard solution.

7.2.2.2. The spike standard is used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

7.2.2.3. Add 250 µL of the spike standard to each 50-mL aliquot of aqueous MS/MSD and LCS/LCSD sample prior to digestion.

7.2.2.4. Add 250 µL of the spike standard to each 10-mL aliquot of mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to dilution and acidification.

7.2.2.5. Add 25 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

7.2.3. Unless specified otherwise, all working standards must be replaced after one month or sooner if comparison with check standards indicates a problem.

7.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

8. CALIBRATION AND STANDARDIZATION

8.1. Top Loading Balance

8.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

8.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

8.2. Thermometer

8.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.3. Pipetter

8.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.4. Dispenser

8.4.1. Calibrate the dispenser according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

9. PROCEDURE

9.1. Unfiltered Aqueous Sample Preparation for Dissolved Mercury Determination

9.1.1. If an aqueous sample was not filtered within 15 minutes of sample collection, filter the sample as soon as possible upon receipt at the laboratory.

9.1.2. Pull the plunger of the syringe and draw a sufficient volume of the aqueous sample into the barrel.

9.1.2.1. For MB/LCS, draw a sufficient volume of clean reagent water.

9.1.2.2. For MS/MSD, draw a sufficient volume of aqueous sample in each analytical batch selected for spiking.

9.1.3. Attach a clean 0.45-µm membrane filter and press the plunger to filter the sample. Record the membrane filter lot (or identification) number in the Acid Preservation and Filtration Logbook.

9.1.4. Collect at least 50 mL of the aqueous sample filtrate in a clean digestion tube and label appropriately. Record the digestion tube lot (or identification) number in the Acid Preservation and Filtration Logbook.

9.1.5. Preserve the aqueous sample filtrate with 1:1 HNO_3 solution to pH < 2 immediately after filtration. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.1.5.1. If the sample will be filtered and then immediately digested, record the filtration information and check the "Filter and Digest" column in the logbook.

9.1.5.2. If the sample will be held after filtration and preservation, and then digested prior to analysis, check the "Filter and Preserve" column in the logbook.

9.1.6. Mix an aqueous sample filtrate thoroughly.

9.1.7. Measure exactly 50 mL of the well-mixed aqueous sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

9.1.7.1. For MB/LCS measure exactly 50 mL of reagent water filtrate designated as MB/LCS.

9.1.7.2. For MS/MSD, measure exactly 50 mL of aqueous sample filtrate designated as MS/MSD.

9.1.8. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.1.9. Proceed to Section 9.7. for digestion procedure.

9.2. Filtered Aqueous Sample Preparation for Dissolved Mercury Determination

9.2.1. Mix an aqueous sample filtrate thoroughly.

9.2.2. Check the pH by transferring a few drops of the aqueous sample filtrate onto a narrow-range pH paper.

9.2.2.1. If the pH is ≥ 2, preserve the aqueous sample filtrate with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.2.2.1.1. Check the "Preserve Only" column in the logbook.

9.2.3. Measure exactly 50 mL of the well-mixed aqueous sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

9.2.3.1. For MB/LCS, measure exactly 50 mL of clean reagent water.

9.2.3.2. For MS/MSD, measure exactly 50 mL of aqueous sample filtrate in each analytical batch selected for spiking.

9.2.4. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.2.5. Proceed to Section 9.7. for digestion procedure.

9.3. Aqueous Sample Preparation for Total Mercury Determination

9.3.1. Mix an aqueous sample thoroughly.

9.3.2. Check the pH by transferring a few drops of the aqueous sample onto a narrow-range pH paper.

9.3.2.1. If the pH is ≥ 2, preserve the aqueous sample with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

9.3.2.1.1. Check the "Preserve Only" column in the logbook.

9.3.3. Measure exactly 50 mL of the well-mixed aqueous sample or exactly 50 mL of the diluted sample into a clean digestion tube. Record the volume of sample used to the nearest 1 mL.

9.3.3.1. For MB/LCS, measure exactly 50 mL of clean reagent water.

9.3.3.2. For MS/MSD, measure exactly 50 mL of aqueous sample in each analytical batch selected for spiking.

9.3.4. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.3.5. Proceed to Section 9.7. for digestion procedure.

9.4. Mobility-Procedure Extract Preparation

9.4.1. Mix a mobility-procedure extract thoroughly.

9.4.2. Measure exactly 10.0 mL of the well-mixed mobility-procedure extract into a clean digestion tube. Record the volume of extract used to the nearest 0.1 mL.

9.4.2.1. For MB/LCS, measure exactly 10.0 mL of mobility-procedure extract designated as MB/LCS. Refer to the mobility extraction method for information.

9.4.2.2. For MS/MSD, measure exactly 10.0 mL of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

9.4.3. Adjust the volume of the mobility-procedure extract to 50 mL with reagent water.

9.4.4. Proceed to Section 9.7. for digestion procedure.

9.5. CRQL Check Standard Preparation

9.5.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

9.5.1.1. For lower limit of quantitation, measure 2.5 µL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water.

9.5.2. Proceed to Section 9.7. for digestion procedure.

9.6. LLOQ Check Sample Preparation

9.6.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 50 mL of reagent water into a clean digestion tube. Mix thoroughly.

9.6.2. Proceed to Section 9.7. for digestion procedure.

9.7. Digestion

9.7.1. Slowly add 2.5 mL of concentrated H_2SO_4 to the digestion tube and mix.

9.7.2. Slowly add 1.25 mL of concentrated HNO_3 to the digestion tube and mix.

9.7.3. Add 7.5 mL of the 5% $KMnO_4$ solution to the digestion tube, and allow the mixture to stand for at least 15 minutes.

9.7.4. Shake and add additional portions of the 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

9.7.4.1. Sewage samples may require additional permanganate.

9.7.4.2. Ensure that equal amounts of permanganate are added to standards and blanks.

9.7.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to the digestion tube.

9.7.6. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

9.7.7. Remove the digestion tube from the block digester and allow the digestate to cool.

9.7.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digestate to reduce excess permanganate.

9.7.9. Adjust the final volume of the digestate to 100 mL with calibration blank.

9.7.10. Transfer a sufficient volume of the digestate to an autosampler vessel and label appropriately. The digestate may now be analyzed.

9.7.10.1. For post digestion spike addition, add 25 µL of the spike standard to 10.0 mL of digestate designated as PDS.

9.8. Thoroughly document all aspects of the digestion in the Mercury Sample Preparation Logbook. This logbook includes, but is not limited to:

9.8.1. Digestion date, start time, and finish time.

9.8.1.1. The start and stop time of each sample digestion must be accurately recorded in the logbook. If all samples were started and finished at the same time, then an 'arrow down' approach may be used in the logbook. If a batch is open, and a sample is added on after the digestion process of the other batch samples has begun, then the actual start and stop time for each additional sample must be recorded in the logbook.

9.8.1.2. All samples must undergo the entire digestion process regardless when the digestion process was started.

9.8.2. Sample matrix, pH, initial volume, and final volume.

9.8.3. Digestion temperature.

9.8.4. Reagent and supply lot (or identification) numbers.

9.8.5. Standard lot (or identification) number, concentration, and volume added.

9.8.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

10. MODIFICATIONS

10.1. The following modifications from EPA Method 7470A are noted.

10.1.1. Reagents and Standards

10.1.1.1. Reagents and standard preparations are modified.

10.1.2. Procedure

10.1.2.1. The volumes of aqueous sample and reagents used for digestion are reduced.

10.1.2.2. The final volume of the digestate is modified.

Appendix B

STANDARD ADDITION PLOT (EXAMPLE)

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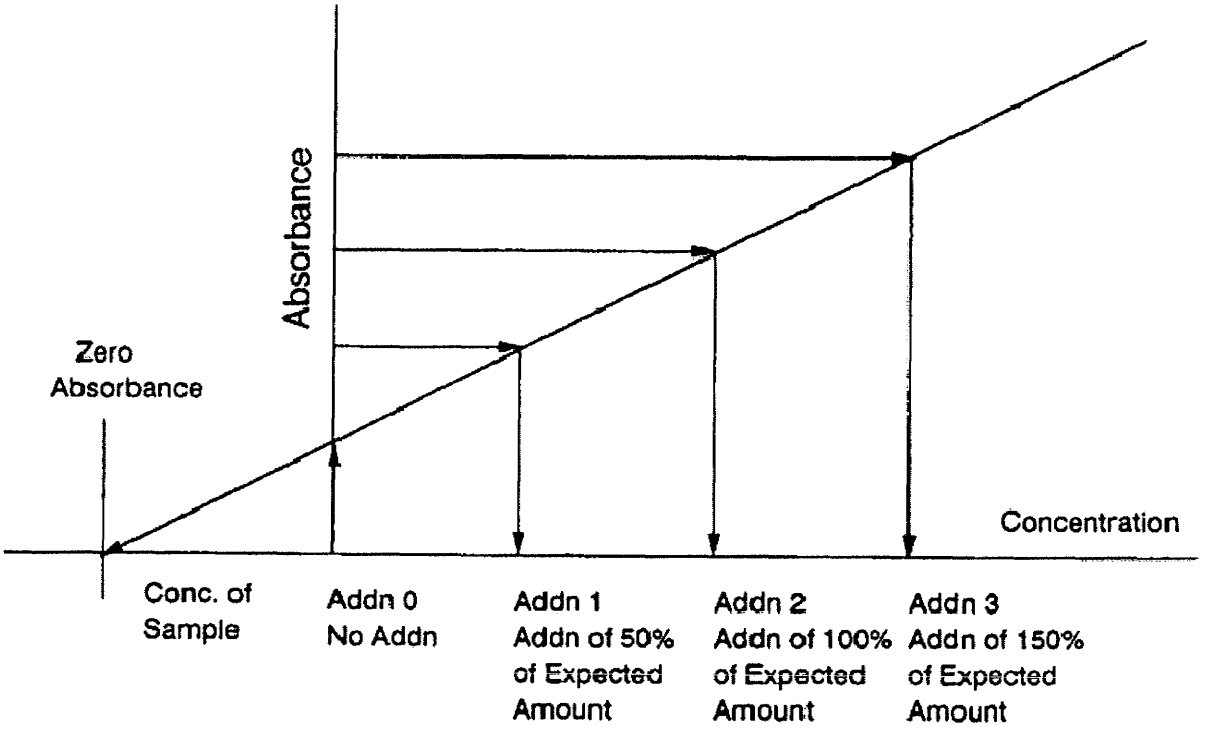
Appendix B

Standard Addition Plot (Example)



Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7470A, Mercury in Liquid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION / QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis.

5.1.2. MDL verification must be performed immediately following an MDL study and quarterly thereafter.

5.1.2.1. MDL verification sample shall be prepared by spiking an appropriate matrix at approximately 2−3 times the detection limit for single-analyte test, or 1−4 times the detection limit for multiple-analyte test.

5.1.2.2. MDL verification is deemed valid if the apparent signal to noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the MDL study and verification at a higher concentration. Set the MDL at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive MDL verifications at a higher concentration. Set the MDL at the higher concentration.

5.1.3. No samples shall be analyzed without a valid MDL.

5.2. Initial Calibration Blank (ICB)

5.2.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > MDL.

5.2.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

5.3. Continuing Calibration Verification (CCV)

5.3.1. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Continuing Calibration Blank (CCB)

5.4.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > MDL.

5.4.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB. Reanalyze all samples since the last acceptable calibration blank.

5.4.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the CCB.

5.5. Event Based Quality Control (LCSs and MBs)

5.5.1. Laboratory Control Samples (LCSs)

5.5.1.1. The lower and upper acceptance limits for %REC of each LCS element in aqueous matrix are 80% and 120%, respectively.

5.5.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.1.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.5.2. Method Blanks (MBs)

5.5.2.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.2.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.2.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.2.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

5.5.2.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6. Matrix Based Quality Control (MS/MSDs)

5.6.1. Matrix Spikes (MS/MSDs)

5.6.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in aqueous matrix are 80% and 120%, respectively. The RPD is ≤ 20%.

5.6.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. ►PROCEDURE

6.1. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Method Blank (MB)
6) Laboratory Control Samples (LCS)
7) Laboratory Control Sample Duplicates (LCSD), ***when required***
8) Samples (up to 10 per batch, including QC check samples and MBs)

9) Continuing Calibration Verification (CCV)
10) Continuing Calibration Blank (CCB)
11) Matrix Spike (MS)
12) Matrix Spike Duplicate (MSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Ending CCV
15) Ending CCB

6.1.1. Item 11: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 12: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix D

EPA METHOD 7470A PROCEDURE OUTLINE

MERCURY IN LIQUID WASTE

Eurofins Calscience, Inc.

EPA METHOD 7470A PROCEDURE OUTLINE

Mercury in Liquid Waste

PROCEDURE

1) Transfer 50 mL of well-mixed aqueous sample into a clean 4-oz digestion tube.
2) Add 2.5 mL of concentrated H_2SO_4.
3) Add 1.25 mL of concentrated HNO_3.
4) Add 7.5 mL of 5% $KMnO_4$ solution (see Note 1).
5) Check for purple color (see Note 2).
6) Add 4 mL of 5% $K_2S_2O_8$ solution.
7) Heat for 2 hours in the water bath at 95°C.
8) Cool and add 3 mL of NaCl-$NH_2OH{\cdot}HCl$ solution.
9) Adjust the final volume to 100 mL with calibration blank.

Note 1: Some samples may require additional 5% $KMnO_4$ solution.

Note 2: Shake and add additional portions of 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

REAGENTS

1) Concentrated H_2SO_4
2) Concentrated HNO_3
3) 5% $KMnO_4$ solution
4) 5% $K_2S_2O_8$ solution
5) NaCl-$NH_2OH{\cdot}HCl$ solution

SAMPLE TYPE QC

1) MB/LCS - per batch of 20 samples
2) MS/MSD - per batch of 20 samples
3) PDS/PDSD - per client/project request

Appendix E

MULTIPLE CALIBRATION STANDARD DIGESTION

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MULTIPLE CALIBRATION STANDARD DIGESTION

1. Initial Calibration Standard Solutions

1.1. Measure 0.01, 0.1, 0.2, 0.5, 1.0 mL of the 1.0-ppm mercury working standard solution and 50 mL of reagent water into five certified clean digestion tubes. Mix thoroughly.

1.2. Slowly add 2.5 mL of concentrated H_2SO_4 to each digestion tube and mix.

1.3. Slowly add 1.25 mL of concentrated HNO_3 to each digestion tube and mix.

1.4. Add 7.5 mL of the 5% $KMnO_4$ solution to each digestion tube, and allow the mixture to stand for at least 15 minutes.

1.5. Add 4.0 mL of the 5% $K_2S_2O_8$ solution to each digestion tube.

1.6. Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with a clean watch glass, and heat for 2 hours in the water bath maintained at 95°C.

1.7. Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.

1.8. Add 3 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solutions to reduce excess permanganate.

1.9. Adjust the volume of the digested standard solutions to 100 mL with calibration blank to obtain 0.025, 0.1, 1.0, 2.0, 5.0 and 10.0 ppb initial calibration standards.

1.10. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.11. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	100*	0.025	100
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.12. *100 ppb standard is diluted from 1.0 ppm working standard daily.

1.13. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

1.14. The initial calibration standard solutions must be prepared fresh daily.

Title : **EPA METHOD 7471A, MERCURY IN SOLID OR SEMISOLID WASTE (COLD-VAPOR TECHNIQUE)**

Document No. : SOP-M620
Revision No. : 3.6
Supersedes : 3.5

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PROPRIETARY INFORMATION STATEMENT

Revision 3.6 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/31/15
MANAGEMENT — DATE

_____ 03-31-15
QA DEPARTMENT — DATE

Reviewer Signature	Review Date	Comments	QA Signature
	03/21/16		

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique).

2. APPLICABLE MATRICES

2.1. This method is applicable to soils, sediments, bottom deposits, and sludge-type materials. It is also applicable to marine and freshwater tissues as a modified method.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Solid	Sediment/Tissue
Mercury	0.0835 mg/kg	0.0200 mg/kg

3.2. The RLs will be proportionally higher for samples which require reduced sample size.

3.3. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

3.4. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 7471A is a cold-vapor atomic absorption procedure for measuring total (organic and inorganic) mercury. All samples must be subjected to an appropriate dissolution step prior to analysis.

4.1.1. If the dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of atomic absorption spectrometer, skilled in the interpretation of atomic absorption spectra, and knowledgeable in the correction of interferences described in this method.

5. METHOD SUMMARY

5.1. Cold-vapor atomic absorption (CVAA) technique is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.2. Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.

5.2.1. Solid, sediment, and tissue samples are digested with acids.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a

product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Terms Specific to Mercury Analysis

6.26.1. Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

6.26.2. Lower Limit of Quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.

6.26.3. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.26.4. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target

analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.26.5. Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration. For atomic absorption, the concentration of metal, in mg/L, that produces a transmission of 1% is commonly employed to determine sensitivity.

6.26.6. Total Mercury: The concentration of mercury determined in a sample following digestion with acids.

7. INTERFERENCES

7.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

7.2. Copper may interfere; however, copper concentrations as high as 10 mg/kg has no effect on the recovery of mercury from spiked samples.

7.3. Samples high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

7.3.1. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 mL).

7.3.2. Free chlorine may be removed by allowing a sample to stand for at least an hour under a hood.

7.4. Certain volatile organic materials that absorb at the wavelength of 253.7 nm may also cause interference.

7.4.1. A preliminary run without reagents may be used to determine whether this type of interference is present.

8. ►SAFETY

8.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Atomic Absorption Spectrometer: PerkinElmer Flow Injection Mercury System (FIMS) 400 or equivalent configured with the following components:

9.1.1. Computer-controlled atomic absorption spectrometer, single-beam optical system, with 254-nm maximum sensitivity.

9.1.2. Solar-blind detector.

9.1.3. Mercury lamp, high intensity, low pressure.

9.1.4. Absorption cell, 240-mm × 7-mm OD × 4-mm ID, quartz.

9.1.5. Two peristaltic pumps, 20–120 rpm variable speed, computer controlled.

9.1.6. Sample loop, 200 µL.

9.1.7. Autosampler, PerkinElmer AS-90 Autosampler or equivalent.

9.1.8. Autosampler vessels, 16-mm OD (15-mL capacity), translucent polypropylene, disposable.

9.1.9. Autosampler vessels, 30-mm OD (50-mL capacity), with screw caps, translucent polypropylene, disposable.

9.2. Instrument Software

9.2.1. PerkinElmer WinLab 32 for AA Version 6.4.0.0191 or equivalent, capable of automatic baseline offset correction.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Carrier Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.5. Graduated cylinders, 100 mL or other capacity, glass, Class A.

9.6. Volumetric flask, 100 mL or other capacity, glass, Class A.

9.7. Pipetters, 100–1000 µL, 0.5–5.0 mL, and 1–10 mL, calibrated, adjustable, with disposable tip.

9.8. Refer to Appendix A for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Chips, Teflon.

10.1.3. Beads, glass.

10.1.4. Hydrochloric acid, HCl, 32−35% or 34−37% (v/v), concentrated, clear colorless liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, or equivalent.

10.1.5. Hydrochloric acid, HCl, 3% (v/v).

10.1.5.1. Prepare the 3% HCl solution by slowly adding 60 mL of concentrated HCl to 500 mL of reagent water and dilute to 2 L with additional reagent water.

10.1.5.2. The 3% HCl solution is used as the carrier solution.

10.1.5.3. It is also used as a rinse blank to flush the system between standards and samples to minimize interferences.

10.1.6. Nitric acid, HNO_3, 67−70% (v/v), concentrated, clear colorless to light yellow liquid, Fisher Scientific TraceMetal or Optima grade, EMD OmniTrace grade, trace metals grade or equivalent.

10.1.7. Stannous chloride, $SnCl_2$, dihydrate, white crystalline powder, reagent grade or equivalent.

10.1.8. Stannous chloride solution, $SnCl_2 \cdot 2H_2O$/HCl.

10.1.8.1. Prepare the stannous chloride solution by adding 11 g of $SnCl_2 \cdot 2H_2O$ to 1 L of 3% HCl solution.

10.1.8.2. The stannous chloride solution is used as the reducing agent.

10.1.9. Refer to Appendix A for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions, 99.990−99.999% source purity, each in sealed polyethylene bottles, containing 1000/100 ppm of mercury are used to prepare calibration and check standards.

10.2.1.2. Prepare each mercury working standard solution by diluting the appropriate volume of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

10.2.1.3. The working standards are prepared as follows:

Analyte	Initial		Final	
	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	1000	0.2	2.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

Analyte	Initial		Final	
	Conc (ppm)	Volume (mL)	Conc (ppm)	Volume (mL)
Hg	100	1.0	1.0	100

Note: The working standard solution contains 5% (v/v) of HNO_3.

10.2.1.4. The working standard solutions must be replaced after one month or sooner if comparison with check standards indicates a problem.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Measure 0.5 mL of the 2.0-ppm mercury working standard solution into a clean digestion tube.

10.2.2.2. Add 10 mL of the diluted aqua regia solution to the digestion tube.

10.2.2.3. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.2.4. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.5. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

10.2.2.6. Mix the contents of the digestion tube thoroughly.

10.2.2.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.2.8. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.2.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.2.10. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 10.0-ppb initial calibration standard.

10.2.2.11. Dilute the appropriate volumes of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain other initial calibration standards.

10.2.2.12. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.13. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	10.0	0.05	20.0
0.25	10.0	0.5	20.0
1.0	10.0	2.0	20.0
2.0	10.0	4.0	20.0
5.0	10.0	10.0	20.0
10.0	10.0	20.0	20.0

10.2.2.14. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

10.2.2.15. The initial calibration standard solutions must be prepared fresh daily.

10.2.3. Calibration Blank (CB)

10.2.3.1. Designate a minimum of five clean digestion tubes for calibration blank preparation.

10.2.3.2. Measure 0.5 mL of reagent water into each clean digestion tube.

10.2.3.3. Add 10 mL of the diluted aqua regia solution to each digestion tube.

10.2.3.4. Place each digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.3.5. Remove the digestion tubes from the block digester and allow the digested reagent water to cool.

10.2.3.6. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to each digestion tube.

10.2.3.7. Mix the contents of each digestion tube thoroughly.

10.2.3.8. Place each digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and

continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.3.9. Remove the digestion tube from the block digester and allow the digested reagent water to cool.

10.2.3.10. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested reagent water to reduce excess permanganate.

10.2.3.11. The CB is used to establish the zero point of the calibration curve or to dilute standards and samples.

10.2.3.12. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.4. Method Blank (MB)

10.2.4.1. Process the MBs using the appropriate sample preparation procedure.

10.2.4.2. The MB is used to identify possible contamination resulting from either the reagents or the equipment used during sample processing.

10.2.5. Initial Calibration Verification (ICV) Solution

10.2.5.1. Measure 0.5 mL of the 1.0-ppm mercury working standard solution into a clean digestion tube.

10.2.5.2. Add 10 mL of the diluted aqua regia solution to the digestion tube.

10.2.5.3. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

10.2.5.4. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.5. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

10.2.5.6. Mix the contents of the digestion tube thoroughly.

10.2.5.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

10.2.5.8. Remove the digestion tube from the block digester and allow the digested standard solution to cool.

10.2.5.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solution to reduce excess permanganate.

10.2.5.10. Adjust the volume of the digested standard solution to 100 mL with calibration blank to obtain the 5.0-ppb ICV solution.

10.2.5.11. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.12. The ICV solution must be prepared fresh daily.

10.2.6. Continuing Calibration Verification (CCV) Solution

10.2.6.1. Dilute 4.0 mL of the 10.0-ppb initial calibration standard to 20 mL with calibration blank to obtain the 2.0-ppb CCV solution.

10.2.6.2. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.6.3. The CCV solution must be prepared fresh daily.

10.2.7. Refer to Appendix A for additional standards.

10.2.8. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures, or 6-in decontaminated brass or stainless steel sleeves with Teflon-lined closures.

11.2. Tissue samples should be collected in 4-oz (or other appropriate capacity) pre-cleaned clear glass or quartz wide-month jars with Teflon or aluminum foil-lined closures. Refer to SOP-M229 for additional information on sample collection, preservation, and containers.

11.3. Solid samples shall be maintained in a chilled state ***(0–6°C)*** post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.4. Tissue samples shall be maintained in a frozen state (≤ −20°C) post sample collection until received at the laboratory. Refer to SOP-M229 for additional information on sample collection and preservation.

11.5. Upon receipt, the solid samples are stored in a 0–6°C cooler, and the tissue samples are stored in a −10 ***through*** −20°C freezer.

11.5.1. Solid and tissue samples must be digested and analyzed within 28 days of sample collection.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established daily prior to the processing of samples.

12.1.1.1. The calibration curve is established with one calibration blank and five or six calibration standards.

12.1.2. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression of each analyte is ≥ 0.995.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.3. Initial Calibration Blank (ICB)

12.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Blank (CCB)

12.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration ≥ RL (or the limit specified in the project specific DQO).

12.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB.

12.6. Contract Required Quantitation Limit (CRQL) Check

12.6.1. A CRQL check standard is analyzed immediately following the ICV/ICB analyses.

12.6.1.1. The concentration of each analyte in the CRQL check solution shall be at the lowest calibration level.

12.6.2. The linearity of the calibration curve is deemed verified if the recovery of each analyte is within 70−130%.

12.6.3. CRQL check is performed per client request or project specific DQOs to verify the linearity of the calibration curve.

12.7. Lower Limit of Quantitation (LLOQ) Check

12.7.1. An LLOQ check sample is analyzed immediately following the ICV/ICB analyses.

12.7.1.1. The concentration of each analyte in the LLOQ check sample is at the established laboratory reporting limit.

12.7.1.2. The LLOQ check sample shall be carried through the entire preparation and analytical procedure.

12.7.2. The lower limit of quantitation is deemed verified if each analyte is detected at within ± 30% of its expected value.

12.7.3. LLOQ check is performed per client request or project specific DQOs to demonstrate the desired detection capability.

12.8. Event Based Quality Control (MBs and LCSs)

12.8.1. ►Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), laboratory control sample ***(LCS)*** and, ***if required***, laboratory control sample duplicate (LCSD).

12.8.1.1. ***An LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.***

12.8.2. The acceptance criteria for MBs are as follows:

12.8.2.1. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific data quality objective (DQO). In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

12.8.2.2. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.8.2.3. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.8.3. The acceptance criteria for LCS elements are as follows:

12.8.3.1. The lower and upper acceptance limits for %REC and RPD of each LCS element are based upon the historical average recovery ± 3S that is updated at least annually.

12.8.3.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.8.3.1.2. The acceptance limits derived from historical data should not be wider than ± 20% for accuracy and 20% for precision.

12.8.3.2. All LCS/LCSD elements must be within acceptance limits. If the LCS/LCSD elements are not acceptable, determine the cause of the problem and effect corrective action.

12.9. Matrix Based Quality Control (MS/MSDs and PDSs)

12.9.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.9.2. The acceptance criteria for MS/MSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.9.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.9.2.1.2. ►The acceptance limits derived from historical data should not be wider than ± ***25%*** for accuracy and 20% for precision.

12.9.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The

MS/MSD data shall be reported with the corresponding sample data.

12.9.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.9.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.10. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.11. Dilution Test

12.11.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.11.2. If this criterion is not met, a chemical or physical interference effect should be suspected. Perform post digestion spike addition.

12.11.3. Dilution test is performed per client request or project specific DQOs.

12.12. Post Digestion Spike Addition

12.12.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10−100 times the RL.

12.12.2. The acceptance criteria for PDS elements are as follows:

12.12.2.1. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

12.12.2.2. If the %REC of a PDS element is not within the established acceptance limits, then matrix effects should be suspected. Perform MSA on all samples in the same preparation batch.

12.12.3. Matrix effects are confirmed if the %REC values of both the MS/MSD and the PDS are unacceptable.

12.12.4. Post digestion spike addition is performed per client request or project specific DQOs.

12.13. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Pipetter

13.1.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.2. Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.

13.2.2.1. Per client request or project specific DQOs, a CRQL check standard must be analyzed immediately following the ICV/ICB analyses to verify the linearity of the calibration curve. The acceptance criteria for the CRQL are listed in Section 12.6.

13.2.2.2. Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the ICV/ICB analyses to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.7.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 15 minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. Use the following CVAA operating conditions as guidance.

Description	Operating Condition
Carrier gas flow	40~70 mL/min
Pump #1 speed	100 rpm
Pump #2 speed	120 rpm
Carrier solution / sample diluent (3.0% HCl)	9~11 mL/min
Reductant (1.1% $SnCl_2$ in 3.0% HCl)	5~7 mL/min
Reaction coil	110-mm × 1.0-mm ID
Wavelength	253.7 nm
Number of replicates	2

14.1.1.2. Autosampler is set to inject 200 µL of field or QC sample digestate.

14.1.2. Place the inlet of the blue/yellow carrier solution pump tube in the hydrochloric acid reservoir. Place the inlet of the red/red reductant pump tube in the stannous chloride reservoir. Position the sampling probe in the reagent water reservoir.

14.1.3. Check the carrier solution and reductant flow rates. The reductant flow rate should be approximately one half of the carrier solution flow rate.

14.1.3.1. Check the flow rate by placing the inlet of the tube in a graduated cylinder filled with reagent water, and then measure the volume decrease after one minute.

14.1.3.2. If the flow rate is not within the appropriate range, adjust the pump pressure for the tube until the flow rate is within range.

14.1.4. Program the system to average two integrations on each blank, standard, and sample. Report the average.

14.1.4.1. If the %RSD for an analyte in a standard is > 10%, document the unacceptable result and reanalyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.4.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, document the unacceptable result and reanalyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish a calibration curve to cover the appropriate concentration range (see Section 13.2.).

14.3. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.

14.3.1. If a failed CCV/CCB is the first of the day, effect corrective action and reanalyze all samples since the last acceptable ICV/ICB.

14.3.2. If a failed CCV/CCB is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.4. Following preparatory procedures specified in Appendix A, the digestates for the QC and actual environmental samples are received in digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels are then loaded onto the system sample tray.

14.5. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) CRQL or LLOQ Check (per client request or project specific DQOs)
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD), ***when required***
9) Samples (up to 10 per batch, including QC check samples and MBs)
10) Continuing Calibration Verification (CCV)
11) Continuing Calibration Blank (CCB)
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)
14) Dilution Test Sample (per client request or project specific DQOs)
15) Post Digestion Spike (PDS) (per client request or project specific DQOs)
16) Samples (up to 10 per batch, including QC check samples and MBs)
17) Ending CCV
18) Ending CCB

14.5.1. Item 1: The CB is an aliquot of reagent water digestate used to establish the zero point of the initial calibration curve.

14.5.2. Item 2: The initial calibration standards are used to establish the initial calibration curve.

14.5.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial multi-point calibration. An acceptable ICV is required daily after initial calibration.

14.5.4. Item 4: The ICB is an aliquot of reagent water digestate used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.5.5. Item 5: The CRQL check standard is used to verify the linearity of the calibration curve. The LLOQ check sample is used to verify the lower limit of quantitation. Per client request or project specific DQOs, an acceptable CRQL or LLOQ check is required immediately following ICV and ICB.

14.5.6. Item 6: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.5.6.1. For solid and tissue samples, the MB consists of clean Teflon chips or glass beads.

14.5.6.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.6.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water digestate must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.5.7. Item 7: The LCS is a known matrix which has been spiked with known concentration of specific target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.5.7.1. For solid and tissue samples, the LCS consists of the specified element spiked into clean Teflon chips or glass beads.

14.5.7.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.8. Item 8: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.9. Items 9 and 16: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.5.9.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.5.10. Items 10 and 17: A CCV is a standard used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily after every batch of 10 samples or portion thereof, and at the end of sequence.

14.5.11. Items 11 and 18: A CCB is an aliquot of reagent water digestate used to monitor contamination. An acceptable CCB is required immediately following CCV.

14.5.12. Item 12: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the

processing of the MS, reagents and procedures identical to those for actual samples are used.

14.5.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.13. Item 13: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.5.14. Item 14: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.5.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.5.14.2. To comply with client request or project specific DQOs, one dilution test sample is required daily for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.15. Item 15: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentration of specific target analyte post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.5.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.5.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.5.16. Rinse blanks consisting of 3% HCl solution may be added elsewhere in the sequence to rinse the analytical system.

14.6. Ensure that sufficient amounts of 3% HCl solution and stannous chloride solution are present in the 3% HCl and stannous chloride reservoirs, respectively, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.7. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7.1. Record the reagent and standard identification numbers on the sequence table printout.

14.8. Initiate the sequence.

14.9. Data Interpretation

14.9.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between absorbances in the sample digestate and the calibration standards.

14.9.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the absorbance of an element can be determined.

14.9.1.2. Determine the concentration based on the initial calibration curve.

14.9.1.2.1. The data system is programmed to perform the calculation of concentration via the Beer-Lambert Law.

14.9.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

14.10. Method of Standard Additions (MSA)

14.10.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.10.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition.

14.10.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the digested reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.9. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or

concentration step is used, the additions are best made first and carried through the entire procedure.

14.10.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix B. A linear regression program may be used to obtain the intercept concentration.

14.10.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.10.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.10.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.10.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{A_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the absorbances for the target analyte.
A_{ave} = mean of the absorbances for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.
Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.6. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in mg.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.7. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in mg.
C_{ss} = solids content in %.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.8. The target analyte concentration for a tissue sample is calculated as follows:

$$C_T = \frac{C_x \times V_x \times D}{W_T}$$

where: C_T = concentration of target analyte in tissue sample in mg/kg.
C_x = concentration of target analyte in digestate in µg/L.
V_x = volume of digestate in mL.
W_T = mass of tissue sample digested in mg.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.
Note: Concentrations and volumes must be in equivalent units.

15.10. All concentrations shall be reported in mg/kg (ppm) for soil and solid waste samples, and mg/kg (ppm) for tissue samples.

15.10.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this

situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analyte in an MB should be less than the respective limit specified in the project specific DQO. In the absence of project specific DQO, the concentration of target analyte in an MB should be less than or equal to one half of the respective RL. If regulatory limit is available, the concentration of target analyte in an MB should be less than 10% of the respective regulatory limit. If the concentration of the target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD elements must be within acceptance limits.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.3. The acceptance criteria for MS/MSD elements vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for

the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 85% and 115%, respectively.

18.4.1. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are confirmed. Perform MSA (see Section 14.10.) on all samples in the same preparation batch.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/kg (ppm) for soil and solid waste samples, and mg/kg (ppm) for tissue samples.

18.7.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ▶CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, ***Quality Control Director***, Quality Control Manager, Group Leader, and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the ***group leader*** confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7471A, USEPA, Revision 1, September 1994.

22.2. *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7471B, USEPA, Revision 2, February 2007.

22.3. *Flame Atomic Absorption Spectrophotometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Inorganic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Sample Preparation and Digestion Procedures.

23.2. Appendix B: Standard Addition Plot (Example).

23.3. Appendix C: Additional Quality Control Criteria for Department of Defense Project.

23.4. ***Appendix D: EPA Method 7471A Procedure Outline***.

23.5. Appendix E: Multiple Calibration Standard Digestion.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 7471A Revision 1 are noted.

Calscience SOP M620 Section	Reference Document EPA Method 7471A Section	Summary of Modification
10.2.	5.7, 5.8, and 7.3	Standard preparations are modified.

24.2. The following modifications from EPA Method 7000B Revision 2 are noted.

Calscience SOP M620 Section	Reference Document EPA Method 7000B Section	Summary of Modification
12.8.2.	9.5	Acceptance criteria of method blank are modified.
12.12.2.	9.8.1	Acceptance criteria of post digestion spike are modified.

25. ▶REVISION HISTORY

Revision	Description	Author(s)	Effective Date
3.4	Section 3: Revise reporting limit terminology, and add reference to MDL determination procedure. Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 12: Clarify quality control criteria. Section 18: Rearrange MB and LCS/LCSD paragraphs. Appendix A Section 7.1.4: Revise aqua regia solution preparation. Appendix A Section 10: List the modifications in table format. Appendix C Section 5: Revise DoD quality control criteria.	K. Chang	06/25/12
3.5	Added Appendix E	X. Xu, L. Lem	08/12/13
3.6	Entire document: Update company name. Section 3: Change EQLs to RLs. Section 6: Update definitions. Sections 8 and 17 and Appendix : Add SDS. Section 11: Update storage temperature. Sections 12, 14, and 18: Update LCSD requirement. Sections 19 and 20: Update responsibilities. Delete (former) Appendix D: Additional Quality Control Criteria for BP Project. Appendix D: Add procedure outline.	L. Hunt	04/06/15

Appendix A

SAMPLE PREPARATION AND DIGESTION PROCEDURES

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique) – Sample Preparation and Digestion Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipment and apparatus required to execute the procedure.

3. METHOD SUMMARY

3.1. EPA Method 7471A provides digestion and cold-vapor atomic absorption conditions for the analysis of mercury in solid or semisolid waste.

4. INTERFERENCES

4.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.2. Samples high in chlorides require additional permanganate (as much as 25 mL) due to the fact that during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

5. ►SAFETY

5.1. Acids are corrosive. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of acids and mercury standards.

5.2. All sample preparation activities must be performed in a fume hood vented to the exterior of the laboratory.

5.2.1. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

5.3. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the digestion.

5.4. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform digestions alone. Another chemist should be present during any digestion process.

5.5. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current

version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Digestion tubes (vials), 4 oz (120 mL), 90-mm × 43-mm ID, graduated, snap closure, with hinged lids, polypropylene, disposable, Capitol Vial P/N 04HPLS or equivalent.

6.2. Watch glass, ribbed or equivalent, glass, appropriate diameter to cover vial.

6.3. Dispensers, 1–10 mL, 2.5–25 mL, and 5–50 mL, calibrated, adjustable.

6.4. Thermometer, calibrated, capable of accurately measuring at 95°C.

6.5. Block digester, equipped with water bath, capable of maintaining 95°C.

6.6. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

6.7. Spatula, PTFE (preferred) or stainless-steel construction.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free, nano-pure.

7.1.2. Chips, Teflon.

7.1.3. Beads, glass.

7.1.4. Diluted aqua regia solution, $HCl/HNO_3/H_2O$, 3:1:4 (v/v/v).

7.1.4.1. Prepare the diluted aqua regia solution by slowly adding 150 mL of concentrated HCl and 50 mL of concentrated HNO_3 to 150 mL of reagent water and dilute to 400 mL with additional reagent water.

7.1.4.2. The diluted aqua regia solution must be prepared immediately prior to use.

7.1.5. Sodium chloride, NaCl, fine white crystals, reagent grade or equivalent.

7.1.6. Hydroxylamine hydrochloride, $H_3NO{\cdot}HCl$, fine white crystalline powder, reagent grade or equivalent.

7.1.7. Sodium chloride-hydroxylamine hydrochloride solution, $NaCl\text{-}H_3NO{\cdot}HCl$.

7.1.7.1. Prepare the sodium chloride-hydroxylamine hydrochloride solution by dissolving 2400 g of NaCl and 2400 g of $H_3NO \cdot HCl$ in reagent water and dilute to 20 L with additional reagent water.

7.1.8. Potassium permanganate, $KMnO_4$, dark purple to green crystals, low mercury (≤ 0.05-ppm Hg), reagent grade or equivalent.

7.1.9. Potassium permanganate, $KMnO_4$, 5% (w/v).

7.1.9.1. Prepare the 5% $KMnO_4$ solution by dissolving 1000 g of $KMnO_4$ in 20 L of reagent water.

7.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. Standards

7.2.1. Stock Standard Solution

7.2.1.1. Pre-certified stock standard solution, 99.990−99.999% source purity, in sealed polyethylene bottle, containing 1000 ppm of mercury is used to prepare check standards.

7.2.1.2. Prepare the 2.0-ppm mercury working standard solution by diluting 0.2 mL of the mercury stock standard and 5 mL of concentrated HNO_3 to 100 mL with reagent water.

7.2.2. Spike Standard Solution

7.2.2.1. Use the 2.0-ppm mercury working standard solution as the spike standard solution.

7.2.2.2. The spike standard is used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

7.2.2.3. Add 250 µL of the spike standard to each 0.6-g aliquot of solid MS/MSD and LCS/LCSD sample prior to digestion.

7.2.2.4. Add 25 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

7.2.3. Unless specified otherwise, all working standards must be replaced after one month or sooner if comparison with check standards indicates a problem.

7.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

8. CALIBRATION AND STANDARDIZATION

8.1. Top Loading Balance

8.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

8.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

8.2. Thermometer

8.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.3. Pipetter

8.3.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

8.4. Dispenser

8.4.1. Calibrate the dispenser according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

9. PROCEDURE

9.1. Solid Sample Preparation

9.1.1. Homogenize a solid, soil, or sediment sample as outlined in the current revision of SOP-M230.

9.1.2. Measure triplicate 0.20-g (wet weight) aliquots (i.e., 0.60-g total) of the homogenized solid sample into a clean digestion tube. Record the mass of sample used to the nearest 0.01 g.

9.1.2.1. For MB/LCS, measure 0.60 ± 0.03 g of clean Teflon chips or glass beads. Record the Teflon chip or glass bead identification number.

9.1.2.2. For MS/MSD, measure 0.60 ± 0.03 g of solid sample in each analytical batch selected for spiking.

9.1.3. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.1.4. Proceed to Section 9.6. for digestion procedure.

9.2. Tissue Sample Preparation

9.2.1. Homogenize marine or freshwater tissue sample as outlined in the current revision of SOP-M229.

9.2.2. Measure 1.00 ± 0.05 g (wet weight) of the homogenized tissue sample into a clean digestion tube. Record the mass of sample used to the nearest 0.01 g.

9.2.2.1. For MB/LCS, measure 1.00 ± 0.05 g of clean Teflon chips or glass beads. Record the Teflon chip or glass bead identification number.

9.2.2.2. For MS/MSD, measure 1.00 ± 0.05 g of tissue sample in each analytical batch selected for spiking.

9.2.3. Add 250 µL of the spike standard solution to all matrix spikes and laboratory control samples.

9.2.4. Proceed to Section 9.6. for digestion procedure.

9.3. CRQL Check Standard Preparation

9.3.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution into a clean digestion tube.

9.3.1.1. For lower limit of quantitation, measure 2.5 µL of the 1.0-ppm mercury working standard solution.

9.3.2. Proceed to Section 9.6. for digestion procedure.

9.4. Solid LLOQ Check Sample Preparation

9.4.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 0.60 ± 0.03 g of Teflon chips or glass beads into a clean digestion tube. Record the Teflon chip or glass bead identification number.

9.4.2. Proceed to Section 9.6. for digestion procedure.

9.5. Tissue LLOQ Check Sample Preparation

9.5.1. Measure 12.5 µL of the 2.0-ppm mercury working standard solution and 1.00 ± 0.05 g of Teflon chips or glass beads into a clean digestion tube. Record the Teflon chip or glass bead identification number.

9.5.2. Proceed to Section 9.6. for digestion procedure.

9.6. Digestion

9.6.1. Add 10 mL of the diluted aqua regia solution to the digestion tube.

9.6.2. Place the digestion tube in the pre-heated block digester, cover the digestion tube with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

9.6.3. Remove the digestion tube from the block digester and allow the digestate to cool.

9.6.4. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to the digestion tube.

9.6.5. Add additional portions of the 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

9.6.5.1. Ensure that equal amounts of permanganate are added to standards and blanks.

9.6.6. Mix the contents of the digestion tube thoroughly.

9.6.7. Place the digestion tube in the pre-heated block digester, cover the digestion tube with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

9.6.8. Remove the digestion tube from the block digester and allow the digestate to cool.

9.6.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digestate to reduce excess permanganate.

9.6.10. Adjust the final volume of the digestate to 100 mL with calibration blank.

9.6.11. Transfer a sufficient volume of the digestate to an autosampler vessel and label appropriately. The digestate may now be analyzed.

9.6.11.1. For post digestion spike addition, add 25 µL of the spike standard to 10.0 mL of digestate designated as PDS.

9.7. Thoroughly document all aspects of the digestion in the Mercury Sample Preparation Logbook. This logbook includes, but is not limited to:

9.7.1. Digestion date, start time, and finish time.

9.7.1.1. The start and stop time of each sample digestion must be accurately recorded in the logbook. If all samples were started and finished at the same time, then an 'arrow down' approach may be used in the logbook. If a batch is open, and a sample is added on after the digestion process of the other batch samples has begun, then the actual start and stop time for each additional sample must be recorded in the logbook.

9.7.1.2. All samples must undergo the entire digestion process regardless when the digestion process was started.

9.7.2. Sample matrix, initial volume, and final volume.

9.7.3. Digestion temperature.

9.7.4. Reagent and supply lot (or identification) numbers.

9.7.5. Standard lot (or identification) number, concentration, and volume added.

9.7.6. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

10. MODIFICATIONS

10.1. The following modifications from EPA Method 7471A Revision 1 are noted.

Calscience SOP M620 Appendix A Section	Reference Document EPA Method 7471A Section	Summary of Modification
7.	5.0 and 7.3	Reagent and standard preparations are modified.
9.6.10.	7.1 and 7.2	The final volume of the digestate is modified.

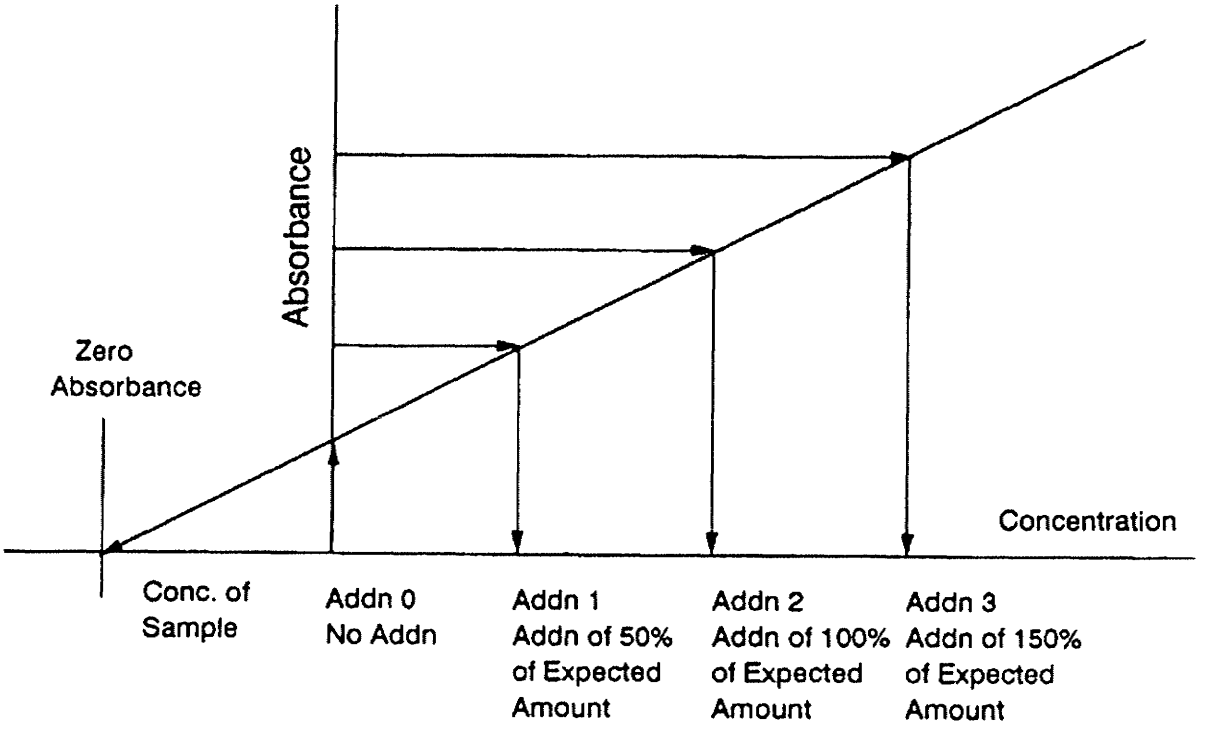
Appendix B

STANDARD ADDITION PLOT (EXAMPLE)

Eurofins Calscience, Inc.

Appendix B

Standard Addition Plot (Example)



Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 7471A, Mercury in Solid or Semisolid Waste (Cold-Vapor Technique) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION / QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration Blank (ICB)

5.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > LOD.

5.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and reanalyze the ICB.

5.4. Continuing Calibration Verification (CCV)

5.4.1. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.5. Continuing Calibration Blank (CCB)

5.5.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > LOD.

5.5.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and reanalyze the CCB. Reanalyze all samples since the last acceptable calibration blank.

5.5.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the CCB.

5.6. Event Based Quality Control (MBs and LCSs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.6.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.6.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCSs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS element in solid matrix are 80% and 120%, respectively.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.2.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control

limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (MS/MSDs)

5.7.1. Matrix Spikes (MS/MSDs)

5.7.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in solid matrix are 80% and 120%, respectively. The RPD is ≤ 20%.

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Method Blank (MB)
6) Laboratory Control Samples (LCS)
7) Laboratory Control Sample Duplicates (LCSD), ***when required***
8) Samples (up to 10 per batch, including QC check samples and MBs)
9) Continuing Calibration Verification (CCV)
10) Continuing Calibration Blank (CCB)
11) Matrix Spike (MS)
12) Matrix Spike Duplicate (MSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Ending CCV
15) Ending CCB

6.1.1. Item 11: The MS is the actual sample matrix spiked with known concentration of specific target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 12: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess

the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix D

EPA METHOD 7471A PROCEDURE OUTLINE

Eurofins Calscience, Inc.

EPA METHOD 7471A PROCEDURE OUTLINE

Mercury in Solid or Semi-Solid Waste

PROCEDURE

1) Measure three 0.20-g aliquots of homogenized solid sample into a clean 4-oz digestion tube.
2) Add 10-mL diluted aqua regia solution.
3) Heat for 2 minutes in the water bath at 95°C.
4) Cool and add 50-mL reagent water.
5) Add 15-mL 5% $KMnO_4$ solution (see Note 1).
6) Check for purple color (see Note 2).
7) Heat for 30 minutes in the water bath at 95°C.
8) Cool and add 6-mL NaCl-H_3NO·HCl solution.
9) Adjust the final volume to 100 mL with calibration blank.

Note 1: Some samples may require additional 5% $KMnO_4$ solution.

Note 2: Shake and add additional portions of 5% $KMnO_4$ solution to the digestion tube, if necessary, until the purple color persists for at least 15 minutes.

REAGENTS

1) Diluted aqua regia solution
2) 5% KMnO4 solution
3) NaCl-H_3NO·HCl solution

SAMPLE TYPE QC

1) MB/LCS - per batch of 20 samples
2) MS/MSD - per batch of 20 samples
3) PDS/PDSD - per client/project request

Appendix E

MULTIPLE CALIBRATION STANDARD DIGESTION

Eurofins Calscience, Inc.

MULTIPLE CALIBRATION STANDARD DIGESTION

1. Initial Calibration Standard Solutions

1.1. Measure 0.01, 0.1, 0.2, 0.5, 1.0 mL of the 1.0-ppm mercury working standard solution and 0.6 g of Teflon® chips into five certified clean digestion tubes. Mix thoroughly.

1.2. Add 10 mL of the diluted aqua regia solution to each digestion tube.

1.3. Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with a clean watch glass, and heat for 2 minutes in the water bath maintained at 95°C.

1.4. Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.

1.5. Add 50 mL of reagent water and 15 mL of the 5% $KMnO_4$ solution to each digestion tube.

1.6. Mix the contents of the digestion tubes thoroughly.

1.7. Place the digestion tubes in the pre-heated block digester, cover the digestion tubes with the same watch glass, and continue to heat for 30 minutes in the water bath maintained at 95°C.

1.8. Remove the digestion tubes from the block digester and allow the digested standard solutions to cool.

1.9. Add 6 mL of the sodium chloride-hydroxylamine hydrochloride solution to the digested standard solutions to reduce excess permanganate.

1.10. Adjust the volume of the digested standard solutions to 100 mL with de-ionized water to obtain the 0.1, 1.0, 2.0, 5.0 and 10.0 ppb initial calibration standards.

1.11. Use the following calibration levels as guidance to prepare the initial calibration standards.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.10	1000	0.01	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.12. Use the following calibration levels as guidance to prepare the initial calibration standards for lower limit of quantitation.

Calibration Level (ppb)	Initial Conc (ppb)	Initial Volume (mL)	Final Volume (mL)
0.025	100*	0.03	100
0.10	1000	0.0	100
1.0	1000	0.1	100
2.0	1000	0.2	100
5.0	1000	0.5	100
10.0	1000	1.0	100

1.13. *100 ppb standard is diluted from 1.0 ppm working standard daily.

1.14. The 2.0-ppb initial calibration standard is also used as the continuing calibration verification solution.

1.15. The initial calibration standard solutions must be prepared fresh daily.

Title : **EPA METHOD 8015B (M), TOTAL PETROLEUM HYDROCARBONS BY GC/FID**

Document No. : SOP-M507
Revision No. : 1.2
Supersedes : 1.1

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PROPRIETARY INFORMATION STATEMENT

Revision 1.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/05/15
MANAGEMENT DATE

_____ 03-05-15
QA DEPARTMENT DATE

Reviewer Signature	Review Date	Comments	QA Signature
	2/19/16		
	3/1/16		
	3/25/16		

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID.

2. APPLICABLE MATRICES

2.1. Aqueous, soil, solids, and sludges.

3. DETECTION / QUANTITATION LIMITS

3.1. Reporting Limits for TPH as Gasoline based on total purgeable hydrocarbons quantitation is 50−100 µg/L for aqueous matrices and 0.5 mg/kg for solid matrices.

3.1.1. Alternate purgeable volatile hydrocarbon types include: Aviation Fuel, Crude Oil.

3.2. Reporting Limits for TPH as Diesel based upon total extractable hydrocarbons quantitation is 50−500 µg/L for aqueous matrices and 5 mg/kg for solid matrices.

3.2.1. Alternate extractable semi-volatile hydrocarbon types include: Crude Oil, Jet A, Jet B, JP4, JP5, Fuel Oil, Generic Fuel Product, Hydraulic Oil, Kerosene, Mineral Oil, Motor Oil, Stoddard Solvent.

3.3. Reporting Limits for Carbon Range analysis based upon total carbon range C7−C36 or C7−C44 quantitation is 50−500 µg/L for aqueous matrices and 5 mg/kg for solid matrices.

3.4. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. This method is used to determine the total concentration of gas chromatographable petroleum-based hydrocarbons in three predominant ranges:

4.1.1. TPH as Gasoline (or other purgeable volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C4 to C12 and covering a boiling point range of < 50−200°C.

4.1.2. TPH as Diesel (or other extractable semi-volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C7 to C28 and covering a boiling point range of about 150−430°C.

4.1.3. Carbon Range corresponding to a range of hydrocarbons from approximately C7 to C44 and covering a boiling point range of < 150−430°C.

4.2. Approximate Analytical Time:

4.2.1. Preparation: < 5 minutes/sample for purge & trap.
30 minutes/sample for extraction.

4.2.2. Analysis: 45 minutes/sample.

5. METHOD SUMMARY

5.1. Samples to be analyzed for Gasoline or other purgeable volatile hydrocarbons are introduced into a gas chromatograph via a purge and trap sample concentrator. Samples to be analyzed for Diesel or other extractable semi-volatile hydrocarbons are solvent extracted and portion of the extract injected directly into a gas chromatograph. The gas chromatograph is temperature programmed to separate the hydrocarbons. Detection is achieved by the use of a flame ionization detector (FID). The samples analyzed for Gasoline are reported based on comparison to a gasoline standard or the specified reference hydrocarbon and samples analyzed for Diesel are reported based on comparison to a diesel standard or the specified reference hydrocarbon.

5.2. Samples analyzed for Carbon Range analysis are analyzed similar to Diesel, use Diesel as the calibration and quantitation standard but have additional straight chain alkane marker standards that serve to provide specific retention ranges that allow quantitation within that range.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***..

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. Each analyst must demonstrate the ability to generate acceptable

results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

7.2. Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that lead to artifacts and/or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferants under the conditions of the analysis by running laboratory method blanks.

7.3. The use of high purity solvents and reagents and pre-conditioning of disposables (i.e., filter paper, boiling stones, extraction thimbles) that come in contact with the sample or extract help to minimize interference problems.

7.4. Contamination by carryover can occur whenever high and low level samples are analyzed sequentially. Suspected high level samples should be analyzed diluted and at the end of the sequence to prevent carryover contamination. In addition, sample syringes, purging devices, and labware should be thoroughly rinsed with solvent between samples.

7.5. Autosampler positional contamination can also occur and can easily go undetected. For an autosampler position that is suspected to contained sample of unusually high concentration, a blank should be analyzed on that position (and the following position) prior to analyzing other samples.

8. ►SAFETY

8.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current ***Eurofins*** Calscience Health & Safety Manual. In general, safety glasses and lab coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Processes that promote vaporization of volatile chemicals into the work area (e.g., separatory shakeout or sonication) should be performed inside an exhaust hood vented to the exterior of the laboratory.

8.4. Material Safety Data Sheets (MSDS) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Purge/Trap Gas Chromatograph: Hewlett Packard 5890 Gas Chromatograph, Hewlett Packard 5890 Series II Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with a

Tekmar LSC 2000 concentrator and an ALS 2016/2032 autosampler or equivalent instrumentation. The system is configured to allow for on-column injections.

9.2. Purge/Trap Gas Chromatographic Column: J&W Scientific DB-5, 30-m × 0.53-mm ID, 1.5-µm film thickness or equivalent.

9.2.1. Use the following operating parameters as guidance for TPH as gasoline analysis.

- Carrier Gas (Nitrogen) flow rate: 8–10 mL/minute
- Makeup Gas (Nitrogen) flow rate: 30 mL/minute
- Injector Temperature: No Injector
- Detector Temperature: 220°C (Manufacturer recommended)
- Temperature Program:
  1. Initial Temperature: 45°C, hold 6 minutes
  2. Program: 45°C to 150°C @ 5°C/minute
  3. Final Temperature/hold: 150°C, hold 2 minutes

9.3. Extractable/Direct Injection Gas Chromatograph: Hewlett Packard 6890 Series Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with Agilent 7683B Series Autosampler or equivalent instrumentation. The system is configured, specifically, for on-column injections.

9.4. Extractable/Direct Injection Gas Chromatographic Column: J&W Scientific DB-5, 10-m × 0.25-mm ID, 0.5- µm film thickness or equivalent.

9.4.1. Use the following operating parameters as guidance for TPH as diesel analysis.

- Carrier Gas (Nitrogen) flow rate: 2–5 mL/minute
- Makeup Gas (Nitrogen) flow rate: 20–25 mL/minute
- Injector Temperature: 280–320°C
- Detector Temperature: 280–320°C
- Temperature Program:
  1. Initial Temperature: 40°C, hold 0.3 minutes
  2. Program: 40°C to 320°C @ 60°C/minute
  3. Final Temperature/hold: 320°C, hold 3–6 minute

9.5. Instrument Software

9.5.1. Requires a PC-based data system or equivalent.

9.5.2. Agilent GC ChemStation Version A.08.03[847], Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.03.02[341], or equivalent.

9.6. Instrument Maintenance and Troubleshooting

9.6.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.6.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.7. Gases

9.7.1. High purity helium (as carrier).

9.7.2. Dry grade air.

9.7.3. Purified hydrogen.

9.7.4. High purity nitrogen (for concentration of extract).

9.8. Kuderna-Danish (KD) apparatus.

9.8.1. Concentrator tubes, 10-mL, ground glass joints.

9.8.2. Snyder columns, three ball macro.

9.8.3. Evaporative flasks, 250-mL.

9.8.4. Concentrator tube holder with nitrogen injectors.

9.9. Shakers

9.9.1. Lab-Line Orbit Shaker or equivalent (aqueous).

9.9.2. Lab-Line Dual Action Shaker or equivalent (solids).

9.10. Analytical balance capable of weighing to the nearest 0.1 g.

9.11. Lab-Line Multi-Unit (Six Station) Extraction Heater.

9.12. Boiling chips, pre-rinsed with solvent.

9.13. Syringes, 10-µL capacity, 5-mL glass gastight, additional volumes as necessary.

9.14. Purging vessels, as specified for purge and trap unit, cleaned.

9.15. 2000-mL glass beakers.

9.16. Vials, 40-mL capacity, equipped with a Teflon-lined screw cap, pre-cleaned.

9.17. Separatory funnels, 1-L and 2-L with Teflon stopcock.

9.18. Fume Hood, exhaust vented from building.

9.19. Ring stands or fume hood hardware to hold separatory funnels.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene Chloride, pesticide grade.

10.1.2. Methanol, purge and trap grade.

10.1.3. Sodium Sulfate, anhydrous, granular.

10.1.4. Silica Gel, 6-12 Mesh (Nominal).

10.1.5. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Refer to the following tables for standard concentrations, alternate spiking levels will be noted where appropriate.

SPIKE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
TPH as Gas	Aqueous	2000	0.005	5.00	mL	5.00	10.0	2.00	2.00
In Methanol (P/T)	Solid	2000	0.005	1.00	g	5.00	10.0	2.00	10.0
TPH as Diesel	Aqueous	20000	0.500	500	mL	25.0	1.20	400	20.0
Extractable in	Solid	20000	0.200	10.0	g	10.0	1.20	400	400
Methylene Chloride	Aqueous	20000	0.100	500	mL	5.00	1.20	400	4.00

SURROGATE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
BFB	Aqueous	500	0.001	5	mL	5.0	0.50	0.1	0.10
In Methanol (P/T)	Solid	500	0.001	1.0	g	5.0	0.50	0.1	0.50
C28	Aqueous	1000	1.25	500.00	mL	25.00	0.15	50.00	2.50
In Methylene Chloride	Solid	1000	0.5	10.00	g	10.00	0.15	50.00	50.0

Note: BFB = 1,4-Bromofluorobenzene; C28 = n-Octacosane

10.2.2. For the previous tables, the following equations apply.

$$\text{Spike Concentration}_{\text{SAMPLE}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Initial Sample Amount (mL or g)}}$$

$$\text{Spike Concentration}_{\text{EXTRACT}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Final Extract Volume (mL)}}$$

10.2.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. Holding times are based on generic guidance in EPA SW-846, Chapter 4, Table 4.1, Update III.

11.2. Samples should be collected in Teflon-lined glass containers with minimal headspace.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Analyzed within 14 days.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	3 × EnCore®	Cool, ≤ 6°C	Extract within 48 hours, Analyzed within 14 days.
	Water	2 × 40 mL	Cool, ≤ 6°C	Analyzed within 14 days, with HCl to pH < 2.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Diesel or other Semi-Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Extract within 14 days, Analyzed within 40 days.
	Water	500−1000* mL	Cool, ≤ 6°C	Extract within 7 days, Analyzed within 40 days.

* Standard aqueous volume is 500 mL; special projects may require 1000 mL.

11.3. Samples submitted with acid preservation should be designated as such on the chain of custody and containers.

11.4. All samples must be iced or refrigerated from the time of collection until extraction or analysis.

11.5. All samples must be extracted and analyzed prior to expiration of the holding time.

11.6. Additional sample quantities may be required for analysis of matrix-specific QC.

11.7. Additional sample handling information can be found in the Sample Control SOPs.

12. ▶QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. Surrogates shall be added to the QC samples.

12.3. The low concentration standard of the initial multipoint calibration should be at or below the applicable reporting limit. When the low concentration standard is above the reporting limit, a spike at the reporting limit shall be analyzed as part of the initial multipoint calibration and documented. The purpose is to verify that detection and quantitation at the reporting limit is achievable.

12.4. Matrix-Based Quality Control (Surrogates and MS/MSDs)

12.4.1. Matrix-based Quality Control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicates (MS/MSD) and surrogates added to each sample.

12.4.2. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is the historical average recovery ±3S.

12.4.2.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.4.2.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This measure alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.4.2.3. By itself, unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.4.2.3.1. Check the surrogate spiking solutions for degradation and contamination.

12.4.2.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample should be re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.4.2.3.2.1. If, upon re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.4.2.3.2.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.4.3. The acceptance criteria for MS/MSDs are as follows:

12.4.3.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.4.3.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.4.3.2.1. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.4.3.2.2. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.5. Event-Based Quality Control (LCSs and MBs)

12.5.1. Event-based quality control consists of QC samples prepared and processed with each batch. This consists of a laboratory control sample and laboratory control sample duplicate (LCS) and a method blank (MB).

12.5.2. The acceptance criteria for LCS compounds vary depending upon historical data. The upper and lower acceptance limits for %REC of each LCS compound are the historical average recovery ±3S. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, the problem must be identified and corrected. The LCS and all associated samples must then be re-analyzed.

12.5.2.1. If the %REC is ***above*** the acceptance limit and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

12.5.2.2. ***An LCS/LCSD shall be prepared whenever there is insufficient sample volume to perform the needed matrix QC (MS/MSD) or as required by project QAPP. In all other instances a single LCS shall be prepared.***

12.5.3. Ideally, the concentration of target analytes in a method blank (MB) should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.5.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect

on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-analyzed.

12.6. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. EXTRACTABLE/ DIRECT INJECTION CALIBRATION

13.1.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.1.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 5, 200, 400, 800, and 1600 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.1.1.2. A ***continuing*** calibration (midpoint) verification (CCV) standard with a %D (between the CCV and initial calibration RFs) being less than or equal to 15%. The RF from the CCV shall be used for quantitation.

13.1.2. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of ***the initial calibration verification (ICV)***, an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.1.3. If CCV does not pass (%D > 15%), it should be reanalyzed. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.2. PURGE AND TRAP CALIBRATION

13.2.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.2.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 0.05, 1.0, 2.0, 5.0, and 10.0 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.2.1.2. A ***continuing*** calibration (midpoint) verification (CCV) standard with a %D (between the CCV and initial calibration RFs) being less than or equal to 15%. The average RF from the initial calibration curve shall be used for quantitation.

13.2.1.2.1. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of ***the initial calibration verification (ICV)***, an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.2.1.2.2. If a CCV does not pass (%D > 15%), it should be reanalyzed.

13.2.1.2.3. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.3. RETENTION TIME WINDOWS

13.3.1. Total Petroleum Hydrocarbons (TPH) are distinguished on the basis of the retention time ranges for the characteristic components in each fuel type.

13.3.2. The retention time range for TPH Gasoline and Diesel is equivalent to the range of the reference standard. Typically there will be an overlap of the upper range of Gasoline with the lower range of Diesel. The EPA 8015B (M) method is modeled on the defunct California DHS LUFT method without the established retention time range markers of the EPA 8015B Method.

13.3.3. Other fuel types will use the characteristic retention time range of the reference standard.

13.3.4. Carbon Chain analysis uses a Diesel standard for Calibration and QC samples with additional Alkane range markers, reference Section 13.3.5.

13.3.5. The retention time for each Carbon-Chain Analysis range is defined during initial calibration and is used to quantitate the hydrocarbons found during analysis. Each range is established from the retention times of the following alkane hydrocarbon markers:

- C5 Pentane
- C6 n-Hexane
- C7 n-Heptane
- C8 n-Octane
- C9 n-Nonane
- C10 n-Decane
- C11 n-Undecane
- C12 n-Dodecane
- C13 n-Tridecane
- C14 n-Tetradecane
- C16 n-Hexadecane
- C18 n-Octadecane
- C20 n-Eicodecane
- C22 n-Docosane

- C23 n-Tricosane
- C24 n-Tetracosane
- C28 n-Octacosane
- C32 n-Dotriacontane
- C36 n-Hexatriacontane
- C40 n-Tetracontane
- C44 n-Tetratetracontane

14. ▶PROCEDURE

14.1. EXTRACTION/DIRECT INJECTION METHOD

14.1.1. SOLID SAMPLE PREPARATION

14.1.1.1. Take a clean 40-mL vial and label it with aqua tape (aqua tape for methylene chloride) and the appropriate sample identification.

14.1.1.2. Place the vial on a top loading balance and tare the balance to zero.

14.1.1.3. Take the appropriate sample, remove the top layer of sample (about ¼ inch) and weigh out 10-g sample into the vial.

14.1.1.4. Add approximately 2-g sodium sulfate and mix with a clean spatula until the sample is "free-flowing". If additional sodium sulfate is required, repeat with additional 2-g portions (not to exceed 10-g. total) of sodium sulfate until sample becomes "free flowing."

14.1.1.5. **OPTIONAL**: Add 1−2-g Silica Gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.1.6. Add 0.5-mL surrogate solution.

14.1.1.7. Add 10-mL of pesticide grade methylene chloride to the vial and tightly cap the vial.

14.1.1.8. Place the vial on shaker machine for 4 minutes. Transfer the methylene chloride layer into clean 40-mL holding vial labeled with the appropriate sample identification.

14.1.1.9. Transfer sufficient concentrated extract into 2-mL autosampler vial for analysis.

14.1.1.10. Store all extracts at 4°C until analysis.

14.1.2. WATER SAMPLE PREPARATION

14.1.2.1. 500-mL Extraction with Partial Concentration

14.1.2.1.1. Take a clean 1-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.1.2. Mark sample container to measure amount of sample provided.

14.1.2.1.3. Shake the sample to homogenize and transfer approximately 500 mL into the separatory funnel.

14.1.2.1.4. Add 25 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.1.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume. Record volume in logbook.

14.1.2.1.6. Add 1.25-mL surrogate solution to sample in separatory funnel.

14.1.2.1.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.1.8. Place in ring stand and allow phases to separation.

14.1.2.1.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction two additional times with 25-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.1.10. Add 5−10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.1.11. **OPTIONAL**: Add 1−2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.1.12. Extract is ready for partial concentration.

14.1.2.1.13. Take entire volume of Methylene Chloride extract and concentrate to 25 mL using a 40-mL glass VOA vial and nitrogen gas injector until level matches reference 25-mL level in second vial used for this purpose.

14.1.2.1.14. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.1.15. Lower reporting levels will require concentration of extract as follows:

14.1.2.1.15.1. For 100-ppb RL = 2.5-mL extract, concentrate to 0.5 mL with 0.25 mL

of surrogate solution, LCS with 0.1-mL solution.

14.1.2.1.15.2. For 50-ppb RL = 5.0-mL extract, concentrate to 0.5 mL with 0.125 mL of surrogate solution, LCS with 0.05-mL solution.

14.1.2.1.15.3. Transfer appropriate amount of extract into a 10-mL K-D concentrator tube labeled with aqua tape and the sample identification.

14.1.2.1.15.4. Place K-D concentrator in nitrogen evaporator apparatus and bubble nitrogen until the proper concentrate volume is achieved. Transfer final extract concentrate in 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.2. 1000-mL Extraction with Full Concentration

14.1.2.2.1. Take a clean 2-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.2.2. Mark sample container to measure amount of sample provided.

14.1.2.2.3. Shake the sample to homogenize and transfer all the sample (assuming 1000-mL sample container) into the separatory funnel.

14.1.2.2.4. Add 60 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.2.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume Record volume on log book.

14.1.2.2.6. Add 0.2-mL surrogate solution to sample in separatory funnel, LCS add 0.05-mL solution.

14.1.2.2.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.2.8. Place in ring stand and allow phases to separation.

14.1.2.2.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction

two additional times with 60-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.2.10. Add 5–10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.2.11. **OPTIONAL**: Add 1–2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.2.12. Extract is ready for full concentration.

14.1.2.2.13. Take entire volume of Methylene Chloride extract and concentrate using 250-mL KD Evaporator Flask, 10-mL Concentrator Tube and 3-Bubble Snyder Column.

14.1.2.2.14. Place in hot bath using 2000-mL beakers filled with water on heating unit.

14.1.2.2.15. Concentrate to 2 mL.

14.1.2.2.16. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.3. Store all extracts and concentrates at 4°C until analysis.

14.1.2.4. For projects that have raised reporting limits, difficult matrices, or suspected to contain high analyte levels, the sample amounts and volumes may be modified as appropriate.

14.1.3. SAMPLE ANALYSIS

14.1.3.1. Program the analytical sequence into the data system.

14.1.3.2. Load one of the extract vials for each sample into the autosampler tray according to the sequence entered into the data system and store duplicate vials at 4°C as backup for potential reanalysis.

14.1.3.3. The extracts are analyzed by direct injection into the E/DI gas chromatograph via the autoinjector.

14.1.3.4. For high level samples where detector saturation is of concern, extract should be diluted to achieve a signal within the quantitation range, preferably near mid calibration range.

14.1.3.5. For samples that have been overdiluted (detector response below the low standard), the sample should be reprepared with less of a dilution to achieve a signal within the quantitation range, preferably near mid calibration range.

14.2. PURGE AND TRAP METHOD

14.2.1. SAMPLE PREPARATION

14.2.1.1. The purge and trap procedure involves minimal sample preparation. A portion of the sample is transferred directly to the purge and trap sample concentrator.

14.2.2. SOIL/SOLID SAMPLE ANALYSIS

14.2.2.1. Place a clean purging vessel on a top loading analytical balance and tare the balance to zero.

14.2.2.2. Take the appropriate sample, remove top layer of sample (about ¼ inch), weigh out 1 g into the clean purging vessel, add 5 mL of reagent water, and add surrogate or spiking compounds when required for the project.

14.2.2.3. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.4. Repeat above steps for all samples in batch.

14.2.2.5. Initiate the analytical sequence.

14.2.2.6. For suspected high level samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.2.2.7. For high level samples where further dilution could result in non-representative aliquots, methanolic extraction followed by P/T of the extract should be performed by the following procedure.

14.2.2.7.1. Take the appropriate sample, remove top layer of sample (about ¼ inch), and weigh out 4 g into a clean 40-mL vial.

14.2.2.8. Add 10 mL of purge and trap grade methanol to the vial and tightly cap.

14.2.2.9. Shake the sample for 2 minutes.

14.2.2.9.1. High Level Samples: Transfer the methanol layer into a small vial minimizing headspace. Label with the appropriate sample identification.

14.2.2.9.2. Dispose 40-mL vial and store extract vial at 4°C until analysis.

14.2.2.10. Using a microsyringe, transfer an aliquot of the extract into a cleaned purging vessel containing 5 mL of water containing surrogate, internal, and, if applicable, matrix spiking standards.

14.2.2.11. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.12. Initiate the analytical sequence.

14.2.3. WATER SAMPLE ANALYSIS

14.2.3.1. Using a 5-mL gastight syringe, transfer 5 mL of the sample into a clean purging vessel and add surrogate or spiking compounds.

14.2.3.2. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.3.3. Repeat above steps for all samples in batch.

14.2.3.4. Initiate the analytical sequence.

14.2.3.5. For medium and high level water samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.3. At the time of sample loading, the pH of each aqueous sample shall be measured with narrow range pH paper to determine if the pH of the sample is < 2 (refer to SOP-T301). The pH range (< 2 or ≥ 2) of each sample shall be documented on the log book.

14.4. The samples are loaded in the following order or in any other acceptable order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 10 per first portion of batch)
5) ***Continuing*** Calibration Verification (CCV)
6) Samples (up to 10 per second portion of batch)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: A CCV is used to verify the acceptance of the initial five point calibration on a continuing basis. An acceptable CCV is required at least every 12 hours and at the end of the sequence.

14.4.1.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

14.4.1.2. In establishing the CCV frequency, all samples and dilutions are counted as sample runs.

14.4.2. Item 2: A LCS is a known matrix that has been spiked with a known concentration of all target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.2.1. For aqueous samples, the LCS consists of the compounds spiked into clean water. For solid samples, the LCS consists of the compounds spiked into washed sea sand.

14.4.2.2. A LCS is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.2.3. The LCSD, ***if required***, is handled identically to the LCS. In addition to assessing the accuracy of the analytical measurement, the LCSD, in combination with the LCS, can be used to assess the precision of the analytical process expressed as relative percent difference (RPD).

14.4.3. Item ***3***: The MB is a known matrix similar to the samples being analyzed that is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.3.1. For aqueous samples, the MB consists of organic free water. For solid samples, the MB consists of washed sea sand.

14.4.3.2. A MB is required with every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs and instrument blanks may be placed in the sequence.

14.4.4. Items ***4 and 6***: Up to 20 samples per batch. High concentration samples should be sufficiently diluted to ensure that instrumentation is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.5. Item ***7***: The MS is the actual matrix spiked with known concentrations of all target analytes. The sample that is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.5.1. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC) of the spiked compounds.

14.4.5.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch".

14.4.6. Item ***8***: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MSD, in combination with the MS, can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

14.4.7. Item ***9***: An acceptable CCV is required at the completion of every analytical sequence.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.6. Initiate the sequence.

15. CALCULATIONS

15.1. Analyte quantitation is accomplished by comparison of chromatographic profile and relative retention times between the sample and retention time range previously established in section 13.3.

15.2. For this method, the data system shall be programmed to integrate the total resolved and unresolved peak area within the retention time range for use in the calculations below. The analyst shall verify and ensure proper baseline integration of all chromatographic output.

15.3. The analyst must identify and record the surrogate area peak. This value is subtracted out of the total chromatographic peak area for each output as detailed in calculations below. In addition, this value is used during data entry so that automated calculations can be performed.

15.4. Standards are prepared using the following formula:

$$\text{Standard Concentration (ppm)} = \frac{\text{Standard Material (µg)}}{\text{Solvent (mL)}}$$

15.5. The response factor (RF) of the reference standard is calculated using the following formula:

$$\text{Response Factor} = \frac{\text{Area Count}_{(\text{STANDARD})} - \text{Area Count}_{(\text{SURROGATE})}}{\text{Standard Concentration (ppm)}}$$

15.6. The sample concentration shall be calculated against the standard reference material for the analyte requested using the following formula:

$$\text{Sample Concentration (ppm)} = \frac{\text{Area Count}_{(\text{SAMPLE})} - \text{Area Count}_{(\text{SURROGATE})}}{RF} \times \frac{V_F}{S} \times DF$$

where: RF = Response factor (AC/ppm)
V_F = Final volume of extract.
S = Amount of sample in mL for liquid (g for solid).
DF = Dilution factor

15.7. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{CF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the average CFs for the target analyte.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.8. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|CF_{ave} - CF|}{CF_{ave}} \times 100$$

where: %D = percent difference of target analyte.
CF = target analyte's daily CF.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.9. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.10. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.11. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.12. Where the chromatographic pattern significantly differs from that of the target standard, the total peak area should be quantitated using the target standard and result qualified to indicate that chromatographic pattern does not match that of the calibration standard.

15.13. Unless specified otherwise by the client, all TPH concentrations will be reported in µg/L (ppb) for aqueous samples and mg/kg (ppm) for solid samples.

15.14. The data reported shall adhere to the significant figures, rounding and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ▶POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS compounds vary depending upon historical data. The upper and lower acceptance limits for %REC of each LCS compound are based upon the historical average recovery ±3S. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS %REC is ***above*** of the acceptance limits and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only ***prepared and analyzed*** when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity ***or when required by project QAPP***.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable

surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for water samples and ***mg/kg (ppm)*** for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS recoveries, to determine acceptance of the sample results.

20.1.2. LCS: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the group leader confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. EPA Method 8000B, Determinative Organic Separations, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

22.2. EPA Method 8015B, Non-Halogenated Organics using GC/FID, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

23. TABLES, DIAGRAMS, FLOWCHARTS AND DATA VALIDATION

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8015B Revision 2 are noted.

Calscience SOP M507 Section	Reference Document EPA Method 8015B Section	Summary of Modification
All	All	Revise criteria for various fuel types.

25. ▶REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.0	Section 3: Revise reporting limits and add reference to detection limits. Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation procedure. Section 13: Insert additional hydrocarbon markers. Section 14: Revise solid sample preparation procedure for extraction/direct injection method, and revise CV to CCV. Section 23: Add Appendix A. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Add DoD requirements.	K. Chang	03/30/12
1.1	Section 9: Update instrument parameters and gas supplies. Section 10: Revise standard preparation procedure. Section 14: Revise solid sample preparation procedure for extraction/direct injection method. Section 25: Add revision history.	I. Kwak / S. Tseng	02/01/13
1.2	Entire document: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 12, 14, and 20: Update LCSD requirement. Section 13: Update CCV criteria. Section 18: Update LCSD requirement and unit. Appendix A: Update LCSD procedure.	L. Hunt	03/16/15

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. ▶DETECTION / QUANTITATION LIMITS

2.1. The ***reporting limits*** must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Retention Time Window

5.4.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.4.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.4.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.5. Event Based Quality Control (MBs and LCS/LCSDs)

5.5.1. Method Blanks (MBs)

5.5.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.5.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.5.2. Laboratory Control Samples (LCS/LCSDs)

5.5.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.2.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.2.2. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.6.1. Surrogates

5.6.1.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall

be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2. Matrix Spikes (MS/MSDs)

5.6.2.1. The RPD is ≤ 30%.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 10 per batch, excluding QC check samples and MBs)
5) ***Continuing Calibration Verification (CCV)***
6) ***Samples (up to 10 per batch, excluding QC check samples and MBs)***
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 1, ***5, and 9***: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Items ***4*** and ***6***: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. Item ***7***: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. Item ***8***: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA METHOD 8081A, ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY**

Document No. : SOP-M400
Revision No. : 5.1
Supersedes : 5.0

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PROPRIETARY INFORMATION STATEMENT

Revision 5.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 04/03/2015
MANAGEMENT **DATE**

_____ 04-03-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature
	5/6/16		

1. METHOD IDENTIFICATION

1.1. EPA Method 8081A, Organochlorine Pesticides by Gas Chromatography.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, oil, soil, and solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Sediment
Pesticides	0.1 µg/L	5 µg/kg (wet-weight)	1 µg/kg (wet-weight)
Chlordane	1.0 µg/L	50 µg/kg (wet-weight)	10 µg/kg (wet-weight)
Toxaphene	2.0 µg/L	100 µg/kg (wet-weight)	20 µg/kg (wet-weight)

	Oil	Wipe/Filter
Pesticides	100 µg/kg	0.1 µg/sample
4,4'-Dichlorobenzophenone		0.5 µg/sample
Chlordane	1000 µg/kg	1.0 µg/sample
Toxaphene	2000 µg/kg	2.0 µg/sample

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8081A is used to determine the concentrations of a number of common organochlorine pesticides in various matrices. The method is used to quantitate organochlorine pesticides without derivitization.

4.2. The following compounds are routinely determined by this method.

aldrin
α-BHC
β-BHC
γ-BHC (lindane)
δ-BHC
α-chlordane
γ-chlordane
chlordane
4,4'-DDD
4,4'-DDE
4,4'-DDT
dieldrin
endosulfan I
endosulfan II
endosulfan sulfate
endrin
endrin aldehyde
endrin ketone
heptachlor
heptachlor epoxide
hexachlorobenzene
methoxychlor
toxaphene

4.3. The following compounds may also be determined by this method.

chlorobenzilate
hexachlorocyclopentadiene

2,4'-DDD (o,p'-DDD)	kepone
2,4'-DDE (o,p'-DDE)	mirex
2,4'-DDT (o,p'-DDT)	cis-nonachlor
diallate	trans-nonachlor
4,4'-dichlorobenzophenone (4,4'-DCBP)	oxychlorodane

4.4. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8081A determination, either by regulatory reference or validation studies.

4.5. Extracts suitable for analysis by this method may also be analyzed for EPA Method 8141, organophosphorus pesticides.

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph (GC) and skilled in the interpretation of gas chromatograms.

5. ►METHOD SUMMARY

5.1. EPA Method 8081A describes chromatographic procedures that will allow for the separation of organochlorine pesticide compounds in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Aqueous samples are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.2. Solid samples are extracted via EPA Methods 3540 or 3550 using methylene chloride-acetone (1:1) exchanged into hexane, or via EPA Method 3545 using ***acetone-hexane (1:1)*** exchanged into hexane.

5.2.3. Solid samples for TCLP, SPLP, or STLC analysis are prepared using the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.4. Oil samples are prepared in accordance with EPA Method 3580 using hexane as the diluent.

5.2.5. A variety of cleanup procedures may be applied to the extracts, depending on the nature of the target analytes and the matrix interferences.

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	Method	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510	SOP-M200
Type of Sample Preparation (Cont.)	**Method**	**SOP No.**
Continuous Liquid-Liquid Extraction	3520	SOP-M201
Soxhlet Extraction	3540	SOP-M203

Pressurized Fluid Extraction	3545	SOP-M204
Ultrasonic Extraction	3550	SOP-M202
Waste Dilution	3580	SOP-M205
Cleanup	3600(M)	SOP-M234
Gel-Permeation Cleanup	3640	SOP-M233
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage. or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.27. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.2. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.2.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2.2. Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition, suspected high level samples may be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.3. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, guard columns should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.4. Endrin and 4,4'-DDT are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection or when the injector contains metal fittings.

7.4.1. Endrin and 4,4'-DDT breakdown to endrin aldehyde, endrin ketone, 4,4'-DDD, or 4,4'-DDE.

7.4.2. When such breakdown is observed, the corrective action may include, but is not limited to 1) cleaning and deactivating the injection port, 2) replacing the injection port liner, or 3) clipping the guard column.

7.5. Phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

7.5.1. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

7.5.2. Exhaustive cleanup of solvents, reagents and glassware may be necessary to eliminate background phthalate ester contamination.

7.6. The presence of sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. EPA Method 3660, Sulfur Cleanup, should be employed for sulfur removal prior to analysis.

7.6.1. The recovery of endrin aldehyde is drastically reduced when using the TBA procedure in EPA Method 3660; hence, this compound must be determined prior to sulfur cleanup when it is an analyte of interest and the TBA procedure is to be used for cleanup.

7.6.2. The use of copper powder technique in EPA Method 3660 may adversely affect the recoveries of some organochlorine compounds and many organophosphorus compounds.

7.7. Waxes, lipids, and other high molecular weight materials can be removed by EPA Method 3640, Gel-Permeation Cleanup.

7.8. Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides.

7.8.1. Certain co-eluting organophosphorus pesticides may be eliminated by the pesticide option of EPA Method 3640.

7.8.2. Co-eluting chlorophenols may be eliminated by EPA Methods 3630 (Silica Gel Cleanup), 3620 (Florisil Cleanup), or 3610 (Alumina Cleanup).

7.9. Polychlorinated biphenyls (PCBs) may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multiple-component analytes such as chlordane and toxaphene. If PCBs are known or expected to occur in samples, consult EPA Methods 3620 and 3630 to separate the pesticides from the PCBs.

7.10. Kepone extracted from samples or in standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to one minute. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality and may seriously affect the ability to identify this compound on the basis of its retention time. As a result, this method is not recommended for determining kepone. EPA Method 8270 may be more appropriate for the analysis of kepone.

8. ►SAFETY

8.1. Compounds covered by this method have been tentatively classified as known or suspected human carcinogens. Primary standards of these compounds must be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

8.4. Refer to the preparatory methods for additional safety issues.

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components:

9.1.1. Autoinjector, Agilent 7683 Series, Agilent 7683B Series, or equivalent.

9.2. Instrument Software

9.2.1. Agilent GC ChemStation Version B.03.01[317], Agilent GC ChemStation Version B.03.02[341], or equivalent.

9.2.2. ***PC-based data system or equivalent.***

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 30-m × 0.32-mm ID, 0.25-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused-silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.8. Carrier Gas: Hydrogen, H_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.9. Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.10. Makeup Gas: Methane, CH_4, 5%, and argon, Ar, 95%, compressed, Praxair P-5 Mixture or equivalent.

9.11. Syringes, 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, and 500 µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.13. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.14. Vial inserts, 300 µL, clear glass, with conical bottom and spring.

9.15. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.16. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 200 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 2 L with additional reagent water.

10.1.5. Methylene chloride (or dichloromethane), CH_2Cl_2, clear colorless liquid, pesticide grade or equivalent.

10.1.6. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.7. Acetone, CH_3COCH_3, clear colorless liquid, pesticide grade or equivalent.

10.1.8. ►***1:1 Acetone / Hexane solvent mixture.***

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing various concentrations of single-component and multi-component pesticide target analyte, and 200 ppm of each surrogate are used to prepare calibration and check standards.

10.2.1.1. Prepare each working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with hexane.

10.2.1.2. The routine single-component pesticide working standards are prepared as follows:

Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
OC pesticides	2000	8.0	4.0	4.0
hexachlorobenzene	100	160		
surrogates	200	160	8.0	

Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
OC pesticides	200	80	4.0	4.0
hexachlorobenzene	100	160		
surrogates	200	160	8.0	

10.2.1.3. The non-routine single-component pesticide working standards are prepared as follows:

Non-Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
2,4'-DDD	100	160	2.0	8.0
2,4'-DDE	100		2.0	
2,4'-DDT	100		2.0	
mirex	100		2.0	
cis-nonachlor	100		2.0	
trans-nonachlor	100		2.0	
oxychlordane	100		2.0	
4,4'-DCBP	500	160	10	
kepone	1000	8.0	2.0	4.0
chlorobenzilate	1000	8.0	2.0	4.0
diallate	1000		2.0	
hexachlorocyclopentadiene	1000		2.0	
surrogates	200	80	4.0	

Non-Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
2,4'-DDD	100	160	2.0	8.0
2,4'-DDE	100		2.0	
2,4'-DDT	100		2.0	
mirex	100		2.0	
cis-nonachlor	100		2.0	
trans-nonachlor	100		2.0	
oxychlordane	100		2.0	
4,4'-DCBP	500	160	10	
kepone	100	80	2.0	4.0
chlorobenzilate	100	80	2.0	4.0
diallate	100		2.0	
hexachlorocyclopentadiene	100		2.0	
surrogates	200	80	4.0	

10.2.1.4. The multi-component pesticide working standards are prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
chlordane	1000	400	100	4.0
toxaphene	1000	400	100	4.0

10.2.2. Pre-certified stock standard solution, in sealed glass ampule, containing 200 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) is used to prepare surrogate working standard.

10.2.2.1. Prepare the 2.0-ppm surrogate working standard solution by diluting 10 mL of the 200-ppm surrogate stock standard to 1.0 L with acetone or other acetone miscible solvent.

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing various concentrations of target analytes are used to prepare spike working standards.

10.2.3.1. Prepare each 1.0-ppm spike working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with acetone or other acetone miscible solvent.

10.2.3.2. The 1.0-ppm spike working standards are prepared as follows:

Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
OC pesticides	200	1.0	1.0	200
hexachlorobenzene	1000	0.2		

Non-Routine Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
2,4'-DDD	100	100	1.0	10
2,4'-DDE	100		1.0	
2,4'-DDT	100		1.0	
mirex	100		1.0	
cis-nonachlor	100		1.0	
trans-nonachlor	100		1.0	
oxychlordane	100		1.0	
4,4'-DCBP	500	100	5.0	
kepone	100	100	1.0	10
chlorobenzilate	100	100	1.0	10
diallate	100		1.0	
hexachlorocyclopentadiene	100		1.0	

10.2.4. Degradation test stock standard solution containing 500 ppm each of 4,4'-DDT and endrin in methanol.

10.2.4.1. Prepare the 500-ppb degradation test working standard solution by diluting 10 µL of the 500-ppm degradation test stock standard to 10 mL with hexane.

10.2.4.2. Prepare the 50-ppb degradation test working standard solution by diluting 4.0 mL of the 500-ppb degradation test working standard to 40 mL with hexane.

10.2.4.3. Inject 2.0 µL of the 50-ppb degradation test working standard for degradation test.

10.2.5. Calibration standard solutions containing various concentrations of target analytes and surrogates in hexane.

10.2.5.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for initial calibration.

10.2.5.2. Use the following calibration levels as guidance to prepare the routine single-component pesticide calibration standards.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
10	20	4.0 + 8.0	10	4.0
20	40	4.0 + 8.0	20	4.0
40	80	4.0 + 8.0	40	4.0
60	120	4.0 + 8.0	60	4.0
80	160	4.0 + 8.0	80	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.5.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide calibration standards.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
10	50	2.0 + 10	40	8.0
20	100	2.0 + 10	80	8.0
40	200	2.0 + 10	160	8.0
60	300	2.0 + 10	240	8.0
80	400	2.0 + 10	320	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
10	20	2.0 + 4.0	20	4.0
20	40	2.0 + 4.0	40	4.0
40	80	2.0 + 4.0	80	4.0
60	120	2.0 + 4.0	120	4.0
80	160	2.0 + 4.0	160	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.5.4. Use the following calibration levels as guidance to prepare the multi-component pesticide calibration standards.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
100	200	100	100	4.0	8.0	4.0	4.0
250	500	100	100	10	20	4.0	4.0
500	1000	100	100	20	40	4.0	4.0
750	1500	100	100	30	60	4.0	4.0
2000	4000	100	100	80	160	4.0	4.0

Note: C = Chlordane; T = Toxaphene

10.2.5.5. The midpoint standards are also used as the continuing calibration verification solutions.

10.2.5.6. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project-specific ***data quality objectives*** (DQO)s.

10.2.6. Initial calibration verification (ICV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.6.1. Dilute the appropriate volumes of the second source working and stock standards to the specified volumes with hexane for initial calibration verification.

10.2.6.2. Use the following calibration level as guidance to prepare the routine single-component pesticide ICV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	40	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.6.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide ICV solutions.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.6.4. Use the following calibration levels as guidance to prepare the multi-component pesticide ICV solutions.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	20	40	4.0	4.0

Note: C = Chlordane; T = Toxaphene

10.2.6.5. The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project-specific DQOs.

10.2.7. Continuing calibration verification (CCV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.7.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for continuing calibration verification.

10.2.7.2. Use the following calibration level as guidance to prepare the routine single-component pesticide CCV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	400	40

Note: A1 = Routine Single-Component Analyte; S = Surrogate

10.2.7.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide CCV solutions.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

10.2.7.4. Use the following calibration levels as guidance to prepare the multi-component pesticide CCV solutions.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	200	400	40	40

Note: C = Chlordane; T = Toxaphene

10.2.7.5. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project-specific DQOs.

10.2.8. Surrogate working standard solution containing 2.0 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or other acetone miscible solvent.

10.2.8.1. Add 500 µL of the 2.0-ppm surrogate working standard to each sample including each quality control (QC) check samples and method blank prior to solvent extraction.

10.2.8.2. Add 500 µL of the 2.0-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.

10.2.9. Spike working standard solutions containing various concentrations of target analytes in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.9.1. Use the 1.0-ppm spike working standard solutions as the single-component pesticide spike working standard solutions. Use the

1000-ppm chlordane stock standard solution and the 1000-ppm toxaphene stock standard solution as the multi-component pesticide spike working standard solutions.

10.2.9.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

10.2.9.3. Add 500 µL of the single-component pesticide spike working standard to each MS/MSD and LCS sample prior to solvent extraction.

10.2.9.4. Per client request or project-specific data quality objectives (DQOs), add 5.0 µL of the chlordane spike working standard to each MS/MSD and LCS sample prior to solvent extraction.

10.2.9.5. Per client request or project-specific DQOs, add 10 µL of the toxaphene spike working standard to each MS/MSD and LCS sample prior to solvent extraction.

10.2.9.6. Add 500 µL of the single-component pesticide spike working standard to each mobility-procedure extract designated as MS/MSD and LCS prior to solvent extraction.

10.2.9.7. Per client request or project-specific DQOs, add 5.0 µL of the chlordane spike working standard to each mobility-procedure extract designated as MS/MSD and LCS prior to solvent extraction.

10.2.9.8. Per client request or project-specific DQOs, add 10 µL of the toxaphene spike working standard to each mobility-procedure extract designated as MS/MSD and LCS prior to solvent extraction.

10.2.10. All working standards must be replaced after six months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.10.1. Store all working standards under dark and refrigerated condition.

10.2.11. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.11.1. Evaluate the toxaphene stock standards carefully. Some toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. As a result, the toxaphene stock standards from different manufacturers may exhibit marked differences which could lead to possible false negative results or to large differences in quantitative results.

10.2.11.2. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. If MS/MSD analyses for single-component pesticide target analytes are required, collect one sample in quadruplicate.

11.1.3. If MS/MSD analyses for multi-component pesticide target analytes are required, collect one sample in quadruplicate, or collect two samples in quadruplicate each.

11.1.4. If MS/MSD analyses for single-component and multi-component pesticide target analytes are required, collect two samples in quadruplicate each, or collect three samples in quadruplicate each.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars, or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Oil, wipe, and filter samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures.

11.4. Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.4.1. If the mobility-procedure extract is known or suspected to contain residual chlorine, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.

11.4.2. Completely fill and hermetically seal the sample container with minimum headspace.

11.5. Aqueous and non-aqueous samples shall be maintained in a chilled state post sample collection until received at the laboratory. Aqueous and non-aqueous samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.5.1. For additional information on aqueous and non-aqueous sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).

11.5.2. For additional information on sample collection and preservation, refer to SOP-M229 and EPA Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Third Edition, Volume 1, Section 6.3.

11.6. Upon receipt, the aqueous and non-aqueous samples are stored in a 0–6°C cooler.

11.6.1. Aqueous samples must be solvent extracted within 7 days of sample collection.

11.6.2. Non-aqueous samples must be solvent extracted within 14 days of sample collection.

11.6.3. Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.

11.6.3.1. Mobility-procedure extracts shall be stored in a 0–6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.

11.6.4. All solvent extracts are then stored under dark and refrigerated (0–6°C) conditions and must be analyzed within 40 days post solvent extraction.

12. ►QUALITY CONTROL

12.1. Degradation Test

12.1.1. Prior to running the calibration standards, the degradation test standard solution must be analyzed and meet the defined acceptance criteria.

12.1.2. The following criteria must be demonstrated every 12 hours.

12.1.2.1. The degradation (or percent breakdown) of 4,4'-DDT and endrin shall be ≤ 15% for each compound. The formula for calculating %B is listed in Section 15.14.

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action, rerun the degradation test, perform injector maintenance, and recalibrate.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

12.2.1.1. The calibration curve is established with a minimum of five calibration standards, but may contain six or seven calibration standards.

12.2.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.3.1. If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.2.3.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.2.3.2.1. In some cases, replace the calibration standard may be necessary.

12.2.3.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.1.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.4.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Retention Time Window

12.5.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.5.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) or ± 0.030 minute, whichever is greater.

12.5.1.1.1. For each multi-component analyte (i.e., chlordane and toxaphene), calculate the standard deviation for each one of the five major characteristic peaks.

12.5.2. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.5.2.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.2.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.5.3. Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:

12.5.3.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.5.3.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.5.3.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.6. Event Based Quality Control (MBs and LCS/LCSDs)

12.6.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)***, and, ***in some cases, a*** laboratory control sample duplicate (LCSD).

12.6.1.1. ***An LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project-specific DQOs.***

12.6.2. The acceptance criteria for MBs are as follows:

12.6.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.6.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.6.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect

on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.6.3. The acceptance criteria for ***LCS or*** LCS/LCSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each LCS compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.6.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.3.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Lower and upper marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.6.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.6.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.6.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.6.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.7.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.7.2. The acceptance criteria for surrogate compounds are as follows:

12.7.2.1. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

12.7.2.1.1. If historical data is available, the lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.7.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound are 60% and 150%, respectively.

12.7.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.7.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.7.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.7.2.4.1. Check the surrogate standard solutions for degradation and contamination.

12.7.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

12.7.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not

caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.7.2.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.7.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.7.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.7.3. The acceptance criteria for MS/MSD compounds are as follows:

12.7.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.7.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.7.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 30%.

12.7.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.7.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.7.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.8. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.9. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Chromatograph Degradation Test

13.2.1. Prior to initial calibration and the analysis of field or QC sample extracts, the GC system must be shown to be resistant to the breakdown of 4,4'-DDT and endrin. The acceptance criteria for the degradation test are listed in Sections 12.1.

13.3. Chromatograph Initial Calibration

13.3.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.3.1.1. Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

13.3.1.2. Recalibration is required for the following maintenance procedures.

13.3.1.2.1. Change, replace, or reverse the analytical column.

13.3.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed

to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.3.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.4. Retention Time Window

13.4.1. Retention time window width for each analyte/surrogate is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.4.2. Document the serial number of the analytical column associated with the retention time window study.

13.4.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

14. ▶PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	pulsed splitless
Inlet temperature	220°C
Inlet pressure	21.579 psi
Total flow rate	90.5 mL/min
Septum purge flow	3 mL/min
Injection pulse pressure	50 psi until 0.3 min
Purge flow to split vent	82.9 mL/min at 2 min
Carrier gas flow rate	4.6 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 200°C at 45°C/min 200°C to 230°C at 12.5°C/min 230°C to 330°C at 20°C/min
Final temperature	330°C, hold 1.9 min

14.1.2. Autoinjector is set to inject 2 µL of field or QC sample extract.

14.1.3. Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion

thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4. and Section 12.5.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.4.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.3. If a failed CCV is not the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. Standard and sample vials are loaded in the following or other logical order:

1) Degradation Test
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 20 per batch, including QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: An acceptable degradation test demonstrates that the chromatographic system is not causing breakdown of thermally labile compounds due to active sites (e.g., the injection port is contaminated or contains catalytic active sites). A degradation test meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.4.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control.

The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand. For wipe samples, the LCS consists of the specified compounds spiked into unused gauze pad. For filter samples, the LCS consists of the specified compounds spiked into unused filter paper. For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD***, if required,*** is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand. For wipe samples, the MB consists of unused gauze pad. For filter samples, the MB consists of unused filter paper. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample (including QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.6.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.7. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.9. Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window for each analyte/surrogate (see Section 12.5.2.1. and Section 12.5.2.2.).

14.8.1.1. Tentative identification of an analyte/surrogate occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.1.1. For each multi-component analyte (i.e., chlordane and toxaphene), choose a minimum of 5 characteristic peaks that are at least 25% of the height of the largest characteristic peak for the analyte, and determine the retention time window of each characteristic peak.

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.5.3.). If any analyte(s)/surrogate(s) in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any analyte(s)/surrogate(s) in the single-component pesticide CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.1.2.2. If any major characteristic peak(s)/surrogate(s) in the multi-component pesticide CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.8.2.1. Multi-component analyte may be quantitated from the total area between the first and last eluting component (total area approach), or the area of 5 or more major characteristic peaks (subset peak approach).

14.8.2.1.1. Total area approach is recommended if the area of the unresolved peaks contributes a significant portion of the area of the total response.

14.8.2.1.2. The reasons for applying total area approach on sample quantitation and the problems associated with sample matrix should be fully documented.

14.8.2.2. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2.1. For multi-component analyte quantitation, a forced baseline or baseline-to-baseline integration across the entire target range is required to ensure the appropriate integration of analyte response.

14.8.2.3. Determine the concentration based on the initial calibration curve.

14.8.2.3.1. Calculate the concentration of each single-component pesticide target analyte in a sample extract using the average of the initial RFs and the area of the characteristic peak. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.2. Calculate the concentration of each multi-component pesticide target analyte in a sample extract using the average of the initial RFs and the total area of the five predetermined peaks. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.3. Refer to Appendix A for examples of the predetermined peaks of each multi-component analyte.

14.8.2.3.4. The data system is programmed to perform the calculation of concentration.

14.8.2.4. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.8.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.8.4.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

14.8.4.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.

14.8.4.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence of chromatographic problems, then it may be appropriate to report the lower result.

14.8.4.1.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.8.4.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.8.4.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.8.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.8.6. Confirmation is required for all positive results unless the samples meet all of the following requirements:

14.8.6.1. All samples (aqueous, solid, or oil) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

14.8.6.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.

14.8.6.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

14.8.6.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

14.8.7. Qualitative confirmation by a second GC column is not required for determining chlordane and toxaphene.

14.8.8. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.8.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.8.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.8.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

14.9. Recommended Instrument Maintenance

14.9.1. Perform the following tasks to remedy the column adsorption problem.

14.9.1.1. Inject an 800-ppb single-component pesticide standard solution to prime (or deactivate) the column.

14.9.1.2. Run one or more solvent blanks consisting of hexane until no carryover is observed prior to analyzing any standards or samples.

14.9.2. Perform the following tasks to eliminate the degradation problem.

14.9.2.1. For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter.

14.9.2.2. Break off the first few centimeters (up to 30 cm) of the injection port side of the column.

14.9.2.3. Check the injector temperature and lower it to 205°C, if necessary.

14.9.2.4. Remove the columns and solvent backflush according to the manufacturer's instructions.

14.9.2.5. If all else fail, it may be necessary to deactivate the metal injector body and/or replace the columns.

14.9.3. Perform the following tasks to rinse the analytical column.

14.9.3.1. Depending on the nature of the residues expected, the first rinse might be reagent water, followed by methanol and acetone, with methylene chloride as the final rinse. In some cases, methylene chloride may be the only solvent necessary.

14.9.3.2. After the final rinse, the analytical column should be filled with methylene chloride and remained flooded overnight to allow materials within the stationary phase to migrate into the solvent.

14.9.3.3. The analytical column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5, 6, or 7 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5, 6, or 7 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS.
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5, 6, or 7 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample solvent extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (oil) sample in µg/kg.

C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (oil) sample solvent extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a wipe (or filter) sample is calculated as follows:

$$C_W = C_{ex} \times V_{ex} \times D$$

where: C_W = concentration of target analyte in wipe (or filter) sample in µg/sample.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in L.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_{MP} = volume of mobility-procedure extract solvent extracted in mL. Unless specified otherwise, V_{MP} = 100.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.13. The percent breakdown is calculated as follows:

15.13.1. The percent breakdown of DDT is calculated as follows:

$$\%B_{DDT} = \frac{A_{DDD} + A_{DDE}}{A_{DDT} + A_{DDD} + A_{DDE}} \times 100$$

where: $\%B_{DDT}$ = percent breakdown of DDT.
A_{DDD} = degradation peak area of DDD.
A_{DDE} = degradation peak area of DDE.
A_{DDT} = peak area of DDT.

15.13.2. The percent breakdown of endrin is calculated as follows:

$$\%B_{endrin} = \frac{A_{aldehyde} + A_{ketone}}{A_{endrin} + A_{aldehyde} + A_{ketone}} \times 100$$

where: $\%B_{endrin}$ = percent breakdown of endrin.
$A_{aldehyde}$ = degradation peak area of aldehyde.
A_{ketone} = degradation peak area of ketone.
A_{endrin} = peak area of endrin.

15.14. Refer to the preparatory method(s) for additional calculations.

15.15. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste samples, and µg/sample for wipe and filter samples.

15.15.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.16. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ▶POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective

apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD ***(when applicable)*** is ≤ 25%. All LCS/LCSD compounds must be within acceptance limits (see Section 12.6.3. for additional information).

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

18.3.1. For EPA Region 9 requirement, refer to Section 12.7.2.1.2. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

18.4.1. For EPA Region 9 requirement, refer to Section 12.7.3.1.2. for acceptance criteria.

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste samples, and µg/sample for wipe and filter samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ►CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, ***Quality Control Director***, Quality Control Manager, Group Leader, and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. ►WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Organochlorine Pesticides by Gas Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8081A, USEPA, Revision 1, December 1996.

22.2. *Determinative Chromatographic Separations,* Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.7. *Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)*, SW-846 Method 8081 or 8080, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Quantitation Peaks for Single-Component and Multi-Component Target Compounds.

23.2. Appendix B: Procedure for Low Limit of Quantitation.

23.3. Appendix C: Additional Quality Control Criteria for Department of Defense Project.

23.4. Appendix D: Control Limits for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8081A Revision 1 are noted.

Calscience SOP M400 Section	Reference Document EPA Method 8081A Section	Summary of Modification
All	All	None.

25. ▶REVISION HISTORY

Revision	Description	Author(s)	Effective Date
5.0	Section 2: Add tissue matrix. Section 3: Update terminology for RL, and add reference to the determinations of DL and RL. Section 4: Revise the scope to indicate routine and non-routine analytes. Update EPA method numbers. Section 5: Update method summary. Section 6: Add LOD and LOQ definitions. Section 7: Update interferences. Section 9: Update the list of equipment and supplies. Section 10: Revise reagent and standard preparations. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Add calibration procedures. Section 14: Update procedures. Section 15: Revise formulas to apply additional calibration levels and add reference to tissue matrix. Section 18: Update section references, and add EPA Region 9 requirements. Section 23: Rearrange the order of appendices. Section 24: Revise modifications. Section 25: Add revision history. Appendix B: Revise the whole appendix for lower limit of quantitation. Appendix C: Update DoD quality control requirements and criteria.	J. Kang / K. Chang	01/04/13

Revision	Description	Author(s)	Effective Date
5.1	Entire document: Update company name. Entire document: Remove tissue matrix. Section 5: Update method 3545 extraction solvent. Section 6: Update definitions. Sections 8 and 17: Add SDS. Section 9: Update equipment. Section 10: Add acetone/hexane. Sections 10, 12, 14, 18, and Appendix C: Update LCSD requirement. Sections 19 and 20: Update responsibilities.	L. Hunt	04/13/15

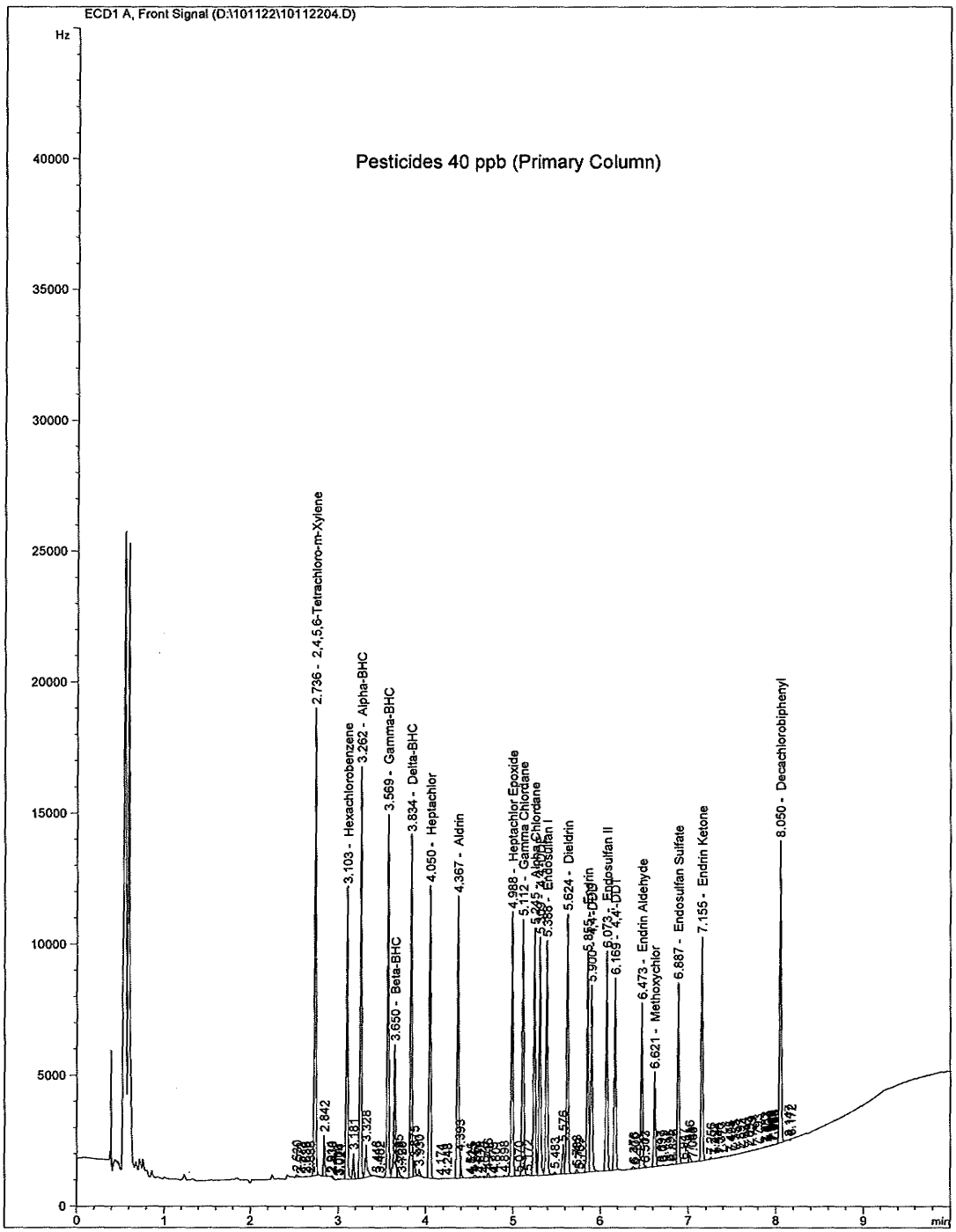
Appendix A

QUANTITATION PEAKS FOR SINGLE-COMPONENT AND MULTI-COMPONENT TARGET COMPOUNDS

Eurofins Calscience, Inc.

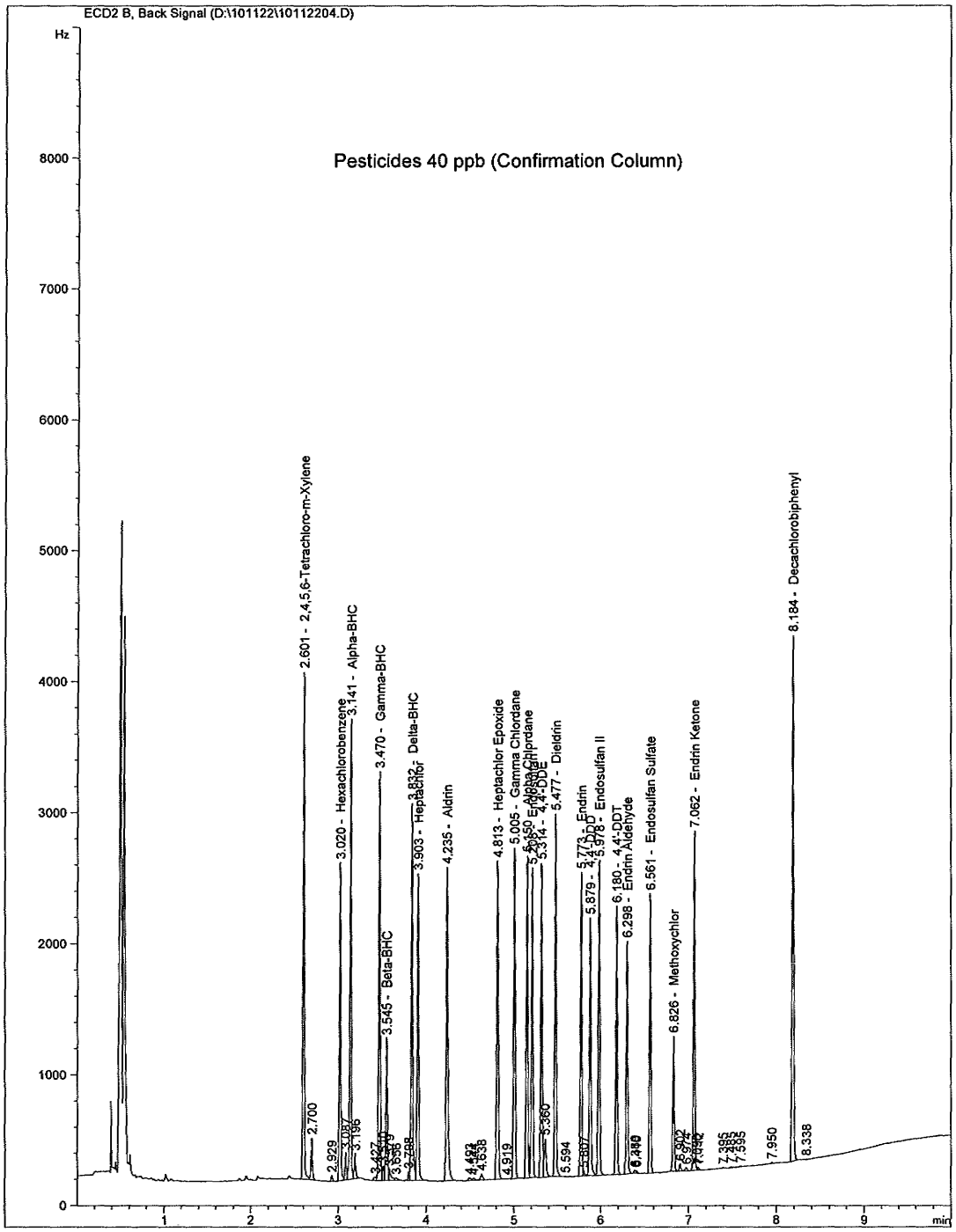
Appendix A

Quantitation Peaks for Single-Component Target Compounds



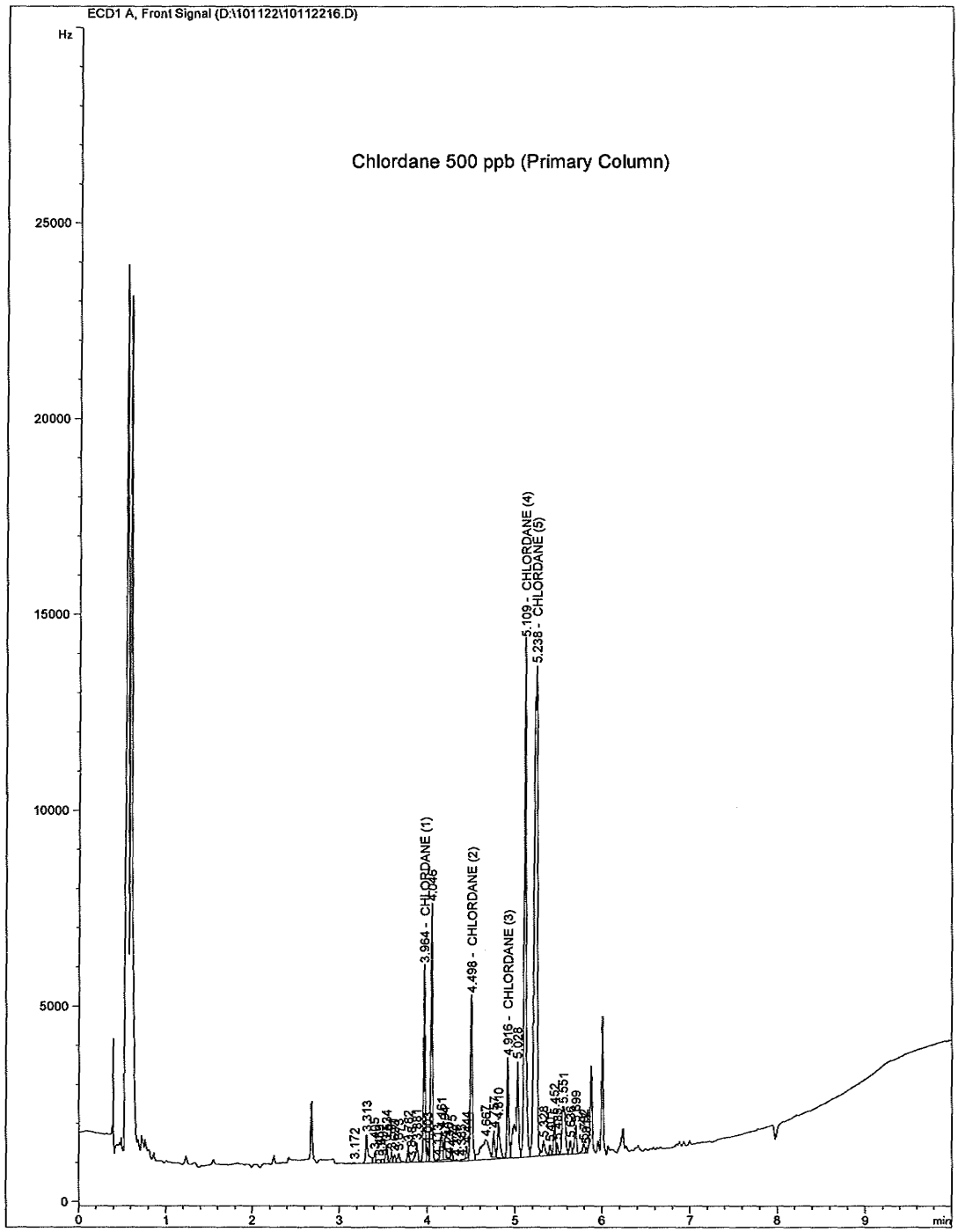
Appendix A

Quantitation Peaks for Single-Component Target Compounds (Cont.)



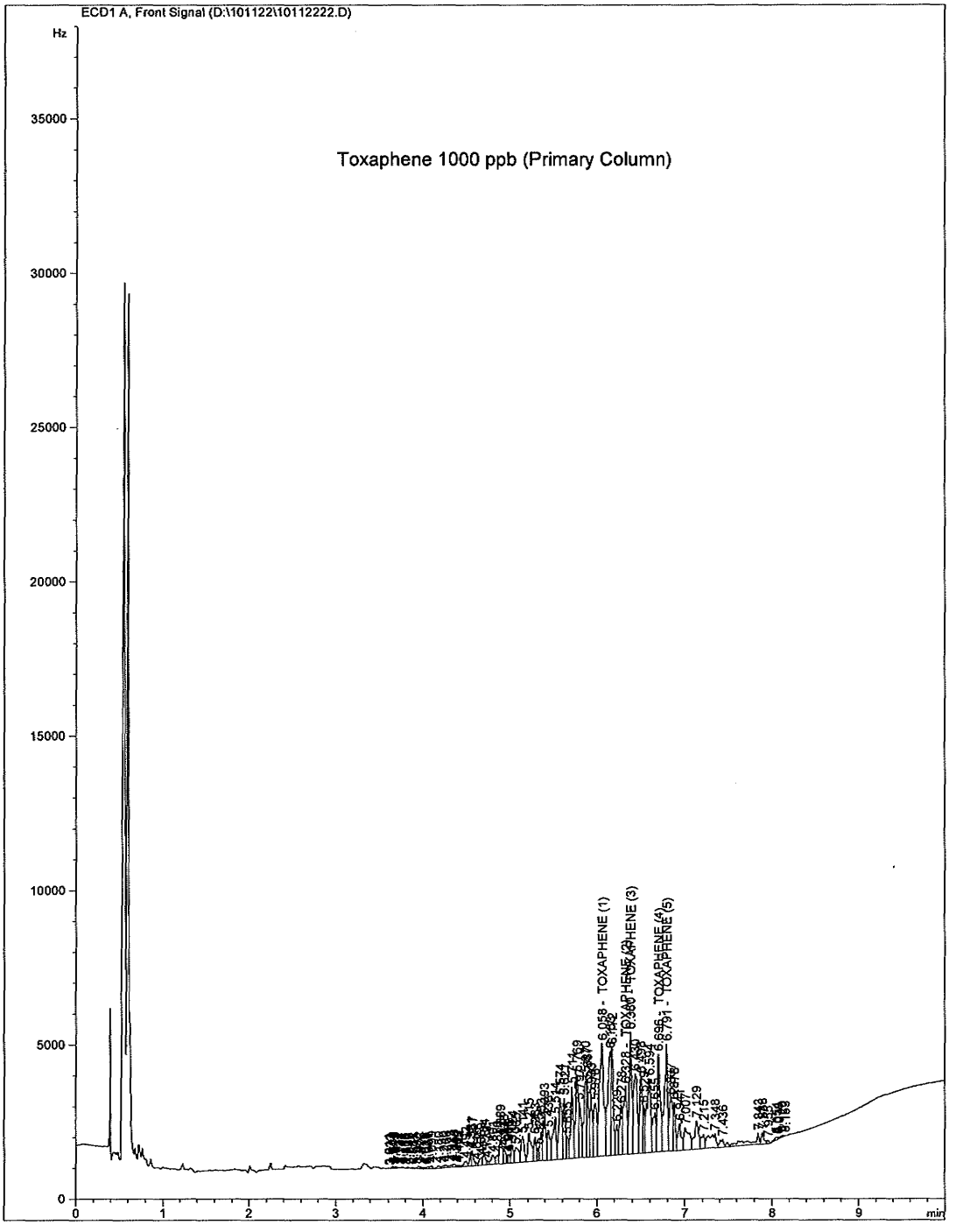
Appendix A

Quantitation Peaks for Multi-Component Target Compounds



Appendix A

Quantitation Peaks for Multi-Component Target Compounds (Cont.)



Appendix B

PROCEDURE FOR LOWER LIMIT OF QUANTITATION

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8081A, Organochlorine Pesticides by Gas Chromatography – Procedure for Lower Limit of Quantitation.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, soil, and solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil
Pesticides	0.010 µg/L	0.2 µg/kg (wet-weight)
Chlordane	0.025 µg/L	0.5 µg/kg (wet-weight)
Toxaphene	0.125 µg/L	2.5 µg/kg (wet-weight)

4. SCOPE AND APPLICATION

4.1. The procedure described herein either supersedes or is in addition to the standard procedure.

5. STANDARDS

5.1. Calibration standard solutions containing various concentrations of target analytes and surrogates in hexane.

5.1.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for initial calibration.

5.1.2. Use the following calibration levels as guidance to prepare the routine single-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
0.5	1.0	4.0 + 8.0	0.5	4.0
2.0	4.0	4.0 + 8.0	2.0	4.0
10	20	4.0 + 8.0	10	4.0
40	80	4.0 + 8.0	40	4.0
60	120	4.0 + 8.0	60	4.0
80	160	4.0 + 8.0	80	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.1.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
2.0	10	2.0 + 10	8.0	8.0
10	50	2.0 + 10	40	8.0
40	200	2.0 + 10	160	8.0
60	300	2.0 + 10	240	8.0
80	400	2.0 + 10	320	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
2.0	4.0	2.0 + 4.0	4.0	4.0
10	20	2.0 + 4.0	20	4.0
40	80	2.0 + 4.0	80	4.0
60	120	2.0 + 4.0	120	4.0
80	160	2.0 + 4.0	160	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.1.4. Use the following calibration levels as guidance to prepare the multi-component pesticide calibration standards for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
5.0		100		0.2		4.0	
10	25	100	100	0.4	1.0	4.0	4.0
100	200	100	100	4.0	8.0	4.0	4.0
500	1000	100	100	20	40	4.0	4.0
750	1500	100	100	30	60	4.0	4.0
2000	4000	100	100	80	160	4.0	4.0

Note: C = Chlordane; T = Toxaphene

5.1.5. The midpoint standards are also used as the continuing calibration verification solutions.

5.1.6. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project-specific DQOs.

5.2. Initial calibration verification (ICV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

5.2.1. Dilute the appropriate volumes of the second source working and stock standards to the specified volumes with hexane for initial calibration verification.

5.2.2. Use the following calibration level as guidance to prepare the routine single-component pesticide ICV solution for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	40	4.0

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.2.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide ICV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.2.4. Use the following calibration levels as guidance to prepare the multi-component pesticide ICV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	20	40	4.0	4.0

Note: C = Chlordane; T = Toxaphene

5.2.5. The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project-specific DQOs.

5.3. Continuing calibration verification (CCV) solutions containing the appropriate concentrations of each target analyte and surrogate in hexane. The CCV solution is of a source same as that used for the initial multi-point calibration.

5.3.1. Dilute the appropriate volumes of the working and stock standards to the specified volumes with hexane for continuing calibration verification.

5.3.2. Use the following calibration level as guidance to prepare the routine single-component pesticide CCV solution for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A1	S	A1 + S	A1 + S	A1 + S
40	80	4.0 + 8.0	400	40

Note: A1 = Routine Single-Component Analyte; S = Surrogate

5.3.3. Use the following calibration levels as guidance to prepare the non-routine single-component pesticide CCV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A2	A3	A2 + A3	A2 + A3	A2 + A3
40	200	2.0 + 10	160	8.0

Note: A2 = Non-Routine Single-Component Analyte; A3 = 4,4'-DCBP

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A4	S	A4 + S	A4 + S	C
40	80	2.0 + 4.0	80	4.0

Note: A4 = Kepone, Chlorobenzilate, Diallate, or Hexachlorocyclopentadiene
S = Surrogate

5.3.4. Use the following calibration levels as guidance to prepare the multi-component pesticide CCV solutions for lower limit of quantitation.

Calibration Level (ppb)		Initial				Final	
		Concentration (ppm)		Volume (µL)		Volume (mL)	
C	T	C	T	C	T	C	T
500	1000	100	100	200	400	40	40

Note: C = Chlordane; T = Toxaphene

5.3.5. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project-specific DQOs.

5.4. Surrogate working standard solution containing 2.0 ppm each of deca-chlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or other acetone miscible solvent.

5.4.1. Add 250 µL of the 2.0-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

5.5. Spike working standard solutions containing various concentrations of target analytes in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

5.5.1. Use the 1.0-ppm spike working standard solutions as the single-component pesticide spike working standard solutions. Use the 1000-ppm chlordane stock standard solution and the 1000-ppm toxaphene stock standard solution as the multi-component pesticide spike working standard solutions.

5.5.2. Add 250 µL of the single-component pesticide spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

5.5.3. Per client request or project-specific data quality objectives (DQOs), add 2.5 µL of the chlordane spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

5.5.4. Per client request or project-specific DQOs, add 5.0 µL of the toxaphene spike working standard to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

6. PROCEDURE

6.1. Aqueous Sample Preparation and Extraction via EPA Method 3510

6.1.1. Prepare and extract an aqueous sample as outlined in SOP-M200 with the following modification on final extract volume.

6.1.1.1. Adjust the final extract volume to 5.0 mL.

6.2. Solid Sample Preparation and Extraction via EPA Method 3545

6.2.1. Prepare and extract a solid sample as outlined in SOP-M204 with the following modifications on sample mass and final extract volume.

6.2.1.1. Measure 50.0 ± 2.5 g of a homogenized solid sample into a clean, pre-assembled extraction cell. Record the mass to the nearest 0.1 g.

6.2.1.1.1. For MB/LCS, measure exactly 50.0 g of washed sea sand. Record the washed sea sand identification number.

6.2.1.1.2. For MS/MSD, measure exactly 50.0 g of solid sample in each analytical batch selected for spiking.

6.2.1.2. Adjust the final extract volume to 5.0 mL.

6.3. Instrument Setup

6.3.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	pulsed splitless
Inlet temperature	220°C
Inlet pressure	21.579 psi
Total flow rate	90.5 mL/min
Septum purge flow	3 mL/min
Injection pulse pressure	50 psi until 0.3 min
Purge flow to split vent	82.9 mL/min at 2 min
Carrier gas flow rate	4.6 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 200°C at 45°C/min 200°C to 230°C at 12.5°C/min 230°C to 330°C at 20°C/min
Final temperature	330°C, hold 1.9 min

Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8081A, Organochlorine Pesticides by Gas Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION / QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Retention Time Window

5.4.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.4.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.4.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.5. Event Based Quality Control (MBs and LCSs)

5.5.1. Method Blanks (MBs)

5.5.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.5.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project-specific data quality objectives (DQOs).

5.5.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.5.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.5.2. Laboratory Control Samples (LCSs)

5.5.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed in Appendix D.

5.5.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.5.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.2.3. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.6.1. Surrogates

5.6.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix D.

5.6.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2. Matrix Spikes (MS/MSDs)

5.6.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix D. The RPD is ≤ 30%.

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. ►PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Degradation Test
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not

contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

6.3.1.2. Follow project-specific reporting requirements when reporting data.

6.3.1.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

6.3.1.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

6.3.2. Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.

7. REFERENCES

7.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix D

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

Appendix D

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
4,4'-DDD	25	150	10	170
4,4'-DDE	35	140	15	160
4,4'-DDT	45	140	30	155
Aldrin	25	140	10	155
α-BHC	60	130	50	140
α-Chlordane	65	125	55	135
β-BHC	65	125	55	135
δ-BHC	45	135	30	150
Dieldrin	60	130	50	140
Endosulfan I	50	110	40	120
Endosulfan II	30	130	10	150
Endosulfan sulfate	55	135	40	150
Endrin	55	135	45	145
Endrin aldehyde	55	135	40	150
Endrin ketone	75	125	70	135
γ-BHC	25	135	10	155
γ-Chlordane	60	125	50	135
Heptachlor	40	130	30	145
Heptachlor epoxide	60	130	50	140
Methoxychlor	55	150	40	165

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix D

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
4,4'-DDD	30	135	10	155
4,4'-DDE	70	125	60	135
4,4'-DDT	45	140	30	155
Aldrin	45	140	30	155
α-BHC	60	125	50	135
α-Chlordane	65	120	55	130
β-BHC	60	125	50	135
δ-BHC	55	130	45	145
Dieldrin	65	125	55	135
Endosulfan I	15	135	10	155
Endosulfan II	35	140	20	160
Endosulfan sulfate	60	135	50	145
Endrin	60	135	50	145
Endrin aldehyde	35	145	20	165
Endrin ketone	65	135	55	145
γ-BHC	60	125	50	135
γ-Chlordane	65	125	55	135
Heptachlor	50	140	35	155
Heptachlor epoxide	65	130	55	140
Methoxychlor	55	145	45	155

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix D

DoD Control Limits of Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
Decachlorobiphenyl	30	135
TMX	25	140

DoD Control Limits of Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
Decachlorobiphenyl	55	130
TMX	70	125

Title : **EPA METHOD 8082, POLYCHLORINATED BIPHENYLS (PCBs) AS AROCLORS BY GAS CHROMATOGRAPHY**

Document No. : SOP-M407
Revision No. : 4.1
Supersedes : 4.0

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PROPRIETARY INFORMATION STATEMENT

Revision 4.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ MANAGEMENT 04/03/15 DATE

_____ QA DEPARTMENT 04-03-15 DATE

Reviewer Signature	Review Date	Comments	QA Signature
	5/6/16		

1. METHOD IDENTIFICATION

1.1. EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, oil, soil, and solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Sediment
PCBs as Aroclors	1.0 µg/L	50 µg/kg (wet-weight)	10 µg/kg (wet-weight)

	Oil	Wipe/Filter
PCBs as Aroclors Aroclor 1221	1000 µg/kg	1.0 µg/sample

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanups.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from various matrices, using a gas chromatographic system configured with a fused-silica capillary column coated with a slightly polar silicone.

4.1.1. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

4.2. The following compounds are routinely determined by this method.

Aroclor-1016	Aroclor-1242	Aroclor-1260
Aroclor-1221	Aroclor-1248	Aroclor-1262
Aroclor-1232	Aroclor-1254	Aroclor-1268

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph (GC) and skilled in the interpretation of gas chromatograms.

5. ►METHOD SUMMARY

5.1. EPA Method 8082 describes chromatographic procedures that will allow for the identification of Aroclors in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Aqueous samples are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.2. Solid samples are extracted via EPA Methods 3540 or 3550 using methylene chloride-acetone (1:1) exchanged into hexane, or via EPA Method 3545 using ***acetone-hexane (1:1)*** exchanged into hexane.

5.2.3. Solid samples for TCLP, SPLP, or STLC analysis are prepared using the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.4. Oil samples are prepared in accordance with EPA Method 3580 using hexane as the diluent.

5.2.5. A variety of cleanup procedures may be applied to the extracts, depending on the nature of the target analytes and the matrix interferences.

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	Method	SOP No.
Separatory Funnel Liquid-Liquid Extraction	EPA 3510	SOP-M200
Continuous Liquid-Liquid Extraction	EPA 3520	SOP-M201
Soxhlet Extraction	EPA 3540	SOP-M203
Pressurized Fluid Extraction	EPA 3545	SOP-M204
Ultrasonic Extraction	EPA 3550	SOP-M202
Waste Dilution	EPA 3580	SOP-M205
Cleanup	EPA 3600(M)	SOP-M234
Gel-Permeation Cleanup	EPA 3640	SOP-M233
TCLP	EPA 1311	SOP-M226
SPLP	EPA 1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and

recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.27. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.2. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.2.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2.2. Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition, suspected high level samples may be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.3. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, a guard column should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.4. Phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

7.4.1. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

7.4.2. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

7.4.3. Phthalate ester interferences may be removed using EPA Method 3665 (Sulfuric Acid/Permanganate Cleanup) prior to analysis.

7.5. Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of EPA Method 3660 (Sulfur Cleanup).

8. ►SAFETY

8.1. Compounds covered by this method have been tentatively classified as known or suspected human carcinogens. Primary standards of these compounds must be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

8.4. Refer to the preparatory methods for additional safety issues.

9. ►EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890 Series Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components.

9.1.1. Autoinjector, Agilent 7680 Series, Agilent 7683 Series, or equivalent.

9.2. Instrument Software

9.2.1. Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.04.02[98], or equivalent.

9.2.2. ***PC-based data system or equivalent.***

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 15-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.8. Carrier Gas: Hydrogen, H_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.9. Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.10. Makeup Gas: Methane, CH_4, 5%, and argon, Ar, 95%, compressed, Praxair P-5 Mixture or equivalent.

9.11. Syringes, 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, and 500 µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.13. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.14. Vial inserts, 300 µL, clear glass, with conical bottom and spring.

9.15. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.16. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 200 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 2 L with additional reagent water.

10.1.5. Methylene chloride (or dichloromethane), CH_2Cl_2, clear colorless liquid, pesticide grade or equivalent.

10.1.6. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.7. Acetone, CH_3COCH_3, clear colorless liquid, pesticide grade or equivalent.

10.1.8. ***1:1 Acetone / Hexane solvent mixture.***

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 100/1000 ppm of each target analyte, and 200 ppm of each surrogate are used to prepare calibration and check standards.

10.2.1.1. Prepare each working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with hexane.

10.2.1.2. The 20-ppm working standards are prepared as follows:

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	100	800	20	4.0
Aroclor 1260	100	800		
surrogates	200	80	4.0	

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	1000	80	20	4.0
Aroclor 1260	1000	80		
surrogates	200	80	4.0	

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1221	100	800	20	4.0
Aroclor 1254	100	800	20	4.0
Aroclor 1232	100	800	20	4.0
Aroclor 1262	100	800	20	4.0
Aroclor 1248	100	800	20	4.0
Aroclor 1268	100	800	20	4.0
Aroclor 1242	100	800	20	4.0
surrogates	200	80	4.0	4.0

10.2.1.3. The 500-ppb working standard is prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppb)	Volume (mL)
Aroclor 1221	100	20	500	4.0
Aroclor 1254	100	20		
Aroclor 1232	100	20	500	4.0
Aroclor 1262	100	20		
Aroclor 1248	100	20	500	4.0
Aroclor 1268	100	20		
Aroclor 1242	100	20	500	4.0

10.2.2. Pre-certified stock standard solution, in sealed glass ampule, containing 200 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) is used to prepare surrogate working standard.

10.2.2.1. Prepare the 2.0-ppm surrogate working standard solution by diluting 10 mL of the 200-ppm surrogate stock standard to 1.0 L with acetone or other acetone miscible solvent.

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing 100/1000 ppm of each target analyte are used to prepare spike working standards.

10.2.3.1. Prepare each 10-ppm spike working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with acetone or other acetone miscible solvent.

10.2.3.2. The 10-ppm spike working standards are prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	1000	2.0	10	200
Aroclor 1260	1000	2.0		
Aroclor 1221	100	1.0	10	10
Aroclor 1254	100	1.0	10	10
Aroclor 1232	100	1.0	10	10
Aroclor 1262	100	1.0	10	10
Aroclor 1248	100	1.0	10	10
Aroclor 1268	100	1.0	10	10
Aroclor 1242	100	1.0	10	10

10.2.4. The calibration standard solution contains various concentrations of target analytes and surrogates in hexane.

10.2.4.1. Dilute the appropriate volumes of the 20-ppm working standards to the specified volumes with hexane for initial calibration.

10.2.4.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
100	20	20 + 4.0	20	4.0
250	50	20 + 4.0	50	4.0
500	100	20 + 4.0	1000	40
750	150	20 + 4.0	150	4.0
2000	400	20 + 4.0	400	4.0

Note: A = Aroclor; S = Surrogate

10.2.4.3. The midpoint standard is also used as the continuing calibration verification solution.

10.2.5. The initial calibration verification (ICV) solutions contain 500 ppb of each target analyte and 100 ppb of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.1. Dilute 100 µL of the second source 20-ppm working standard to 4.0 mL with hexane for initial calibration verification.

10.2.5.2. Use the following calibration level as guidance to prepare the ICV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	100	4.0

Note: A = Aroclor; S = Surrogate

10.2.6. The continuing calibration verification (CCV) solution contains 500 ppb of each target analyte and 100 ppb of each surrogate in hexane. The CCV solution is of a source same as that used for the initial five-point calibration.

10.2.6.1. Dilute 1000 µL of the 20-ppm working standard to 40 mL with hexane for continuing calibration verification.

10.2.6.2. Use the following calibration level as guidance to prepare the CCV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	1000	40

Note: A = Aroclor; S = Surrogate

10.2.7. The surrogate working standard solution contains 2.0 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or other acetone miscible solvent.

10.2.7.1. Add 500 µL of the 2.0-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

10.2.7.2. Add 500 µL of the 2.0-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.

10.2.8. The spike working standard solution contains 10 ppm of each target analyte in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. Use the 10-ppm spike working standard solution containing only Aroclor 1016 and Aroclor 1260 if samples are not expected to contain any Aroclor. Use the 10-ppm spike working standard solution containing the specific Aroclor(s) if samples are expected to contain these Aroclor(s).

10.2.8.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.3. Add 200 µL of the spike working standard containing only Aroclor 1016 and Aroclor 1260 to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

10.2.8.4. Per client request or project-specific data quality objectives (DQOs), add 200 µL of the spike working standard containing the specific Aroclor(s) to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

10.2.8.5. Add 200 µL of the spike working standard containing only Aroclor 1016 and Aroclor 1260 to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.

10.2.8.6. Per client request or project-specific DQOs, add 200 µL of the spike working standard containing the specific Aroclor(s) to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.

10.2.9. All working standards must be replaced after six months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.9.1. Store all working standards under dark and refrigerated condition.

10.2.10. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.10.1. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. If MS/MSD analyses are required, collect one sample in quadruplicate.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars, or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Oil, wipe, or filter samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures.

11.4. Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.4.1. If the mobility-procedure extract is known or suspected to contain residual chlorine, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.

11.4.2. Completely fill and hermetically seal the sample container with minimum headspace.

11.5. Aqueous and non-aqueous samples shall be maintained in a chilled state post sample collection until received at the laboratory. Aqueous and non-aqueous samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.5.1. For additional information on aqueous and non-aqueous sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).

11.5.2. For additional information on sample collection and preservation, refer to SOP-M229 and EPA Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Third Edition, Volume 1, Section 6.3.

11.6. Upon receipt, the aqueous and non-aqueous samples are stored in a 0–6°C cooler.

11.6.1. Aqueous samples must be solvent extracted within 7 days of sample collection.

11.6.2. Non-aqueous samples must be solvent extracted within 14 days of sample collection.

11.6.3. Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.

11.6.3.1. Mobility-procedure extracts shall be stored in a 0–6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.

11.6.4. All solvent extracts are then stored under dark and refrigerated (0–6°C) conditions and must be analyzed within 40 days post solvent extraction.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established prior to the processing of sample extracts.

12.1.1.1. The calibration curve is established with a minimum of five calibration standards.

12.1.1.1.1. A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. Hence, it is not necessary to establish the initial five-point calibration for each of the other Aroclors.

12.1.1.1.2. In situations where only a few Aroclors are of interest for a specific project, it will be necessary to

establish the initial five-point calibration for each Aroclor of interest.

12.1.1.2. If the calibration curve is not established for each Aroclor other than Aroclor 1016 and Aroclor 1260, analyze the 500-ppb working standards for pattern recognition.

12.1.1.2.1. The 500-ppb working standards may also be used to determine the single-point calibration factor for each Aroclor if both of the following conditions are met.

12.1.1.2.1.1. The linearity of the detector response is demonstrated using the calibration standards containing only Aroclor 1016 and Aroclor 1260.

12.1.1.2.1.2. The calibration option is linear least squares regression and the regression is forced through zero.

12.1.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.3.1. If the RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.1.3.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.1.3.2.1. In some cases, replace the calibration standard may be necessary.

12.1.3.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-analysis.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.1.1. For EPA Region 9 requirement, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.4. Retention Time Window

12.4.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) or ± 0.030 minute, whichever is greater.

12.4.1.1.1. For each multi-component analyte (i.e., Aroclor), calculate the standard deviation for each one of the five major characteristic peaks.

12.4.2. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.

12.4.2.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.2.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.3. Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:

12.4.4. Retention time window for each analyte/surrogate is verified as follows:

12.4.4.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.4.4.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.4.4.3. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.

12.5. Event Based Quality Control (MBs and LCSs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)***, and, ***in some cases, a*** laboratory control sample duplicate (LCS).

12.5.1.1. ***An LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project-specific DQOs.***

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.5.3. The acceptance criteria for ***LCS or*** LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC of each LCS compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.5.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.2. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, determine the cause of the problem and effect corrective action.

12.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.6.2. The acceptance criteria for surrogate compounds are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

12.6.2.1.1. If historical data is available, the lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound are 60% and 150%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate

recoveries, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for MS/MSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.6.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 30%.

12.6.3.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The

MS/MSD data shall be reported with the corresponding sample data.

12.6.3.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Chromatograph Initial Calibration

13.2.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.1.1. Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

13.2.1.2. Recalibration is required for the following maintenance procedures.

13.2.1.2.1. Change, replace, or reverse the analytical column.

13.2.2. After obtaining an acceptable five-point calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.2.3. The initial five-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.3. Retention Time Window

13.3.1. Retention time window width for each analyte/surrogate is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up, following column changes, after major instrument maintenance or when a significant retention time shift is suspected.

13.3.2. Document the serial number of the analytical column associated with the retention time window study.

13.3.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

14. ►PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	splitless
Inlet temperature	220°C
Inlet pressure	6.2041 psi
Total flow rate	87.6 mL/min
Carrier gas flow rate	1.7 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 300°C at 15°C/min
Final temperature	300°C, hold 15 min

14.1.2. Autoinjector is set to inject 2 µL of field or QC sample extract.

14.1.3. Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence. If the QC and retention time criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.3. If a failed CCV is not the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. Standard and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 20 per batch, including QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: The IB is a vial of hexane used to determine whether the GC system is free of interferants. Additional instrument blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples). IB is optional.

14.4.2. Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand. For wipe samples, the LCS consists of the specified compounds spiked into unused gauze pad. For filter samples, the LCS consists of the specified compounds spiked into unused filter paper. For mobility-procedure extracts,

the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD***, if required,*** is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand. For wipe samples, the MB consists of unused gauze pad. For filter samples, the MB consists of unused filter paper. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of hexane must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample (including QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.6.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.7. Item 7: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for

the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.4.9. Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Establish the daily retention time window for each analyte/surrogate (see Section 12.4.2.1. and Section 12.4.2.2.).

14.8.1.1. Tentative identification of an analyte/surrogate occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.1.1. For each multi-component analyte (i.e., Aroclor), choose a minimum of 5 characteristic peaks that are at least 25% of the height of the largest characteristic peak for the analyte, and determine the retention time window of each characteristic peak.

14.8.1.1.2. The set of peaks for each Aroclor should include at least one peak that is unique to that Aroclor.

14.8.1.1.2.1. For Aroclor 1016 and Aroclor 1260, none of the peaks chosen should be found in both of these Aroclors.

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any analyte(s)/surrogate(s) in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any major characteristic peak(s)/surrogate(s) in the CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.1.3. For Aroclors other than Aroclor 1016 and Aroclor 1260, identification shall rely primarily on pattern recognition. However, retention times should be utilized as a guide.

14.8.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample extract and the calibration standards.

14.8.2.1. PCBs as Aroclor may be quantitated from the total area of the PCB pattern and on the basis of the Aroclor standard that is most similar to the sample (total area approach), or the area of 5 or more major characteristic peaks (subset peak approach).

14.8.2.1.1. If total area approach is employed, any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area.

14.8.2.1.2. Total area approach is recommended if weathering of PCBs in the environment and changes resulting from waste treatment processes alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable, or if samples contain more than one Aroclor.

14.8.2.1.3. The reasons for applying total area approach on sample quantitation and the problems associated with sample matrix should be fully documented.

14.8.2.2. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2.1. For multi-component analyte quantitation, a forced baseline or baseline-to-baseline integration across the entire target range is required to ensure the appropriate integration of analyte response.

14.8.2.3. Determine the concentration based on the initial calibration curve.

14.8.2.3.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the total area of the five predetermined peaks. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.2. Refer to Appendix A for examples of the predetermined peaks of each multi-component analyte.

14.8.2.3.3. The data system is programmed to perform the calculation of concentration.

14.8.2.4. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.8.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.8.4.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

14.8.4.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.

14.8.4.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence

of chromatographic problems, then it may be appropriate to report the lower result.

14.8.4.1.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.8.4.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.8.4.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.8.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.8.6. Confirmation is required for all positive results unless the samples meet all of the following requirements:

14.8.6.1. All samples (aqueous, solid, ***or*** oil) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

14.8.6.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.

14.8.6.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

14.8.6.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

14.8.7. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.7.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.7.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.7.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

14.9. Recommended Instrument Maintenance

14.9.1. Perform the following tasks to remedy the column adsorption problem.

14.9.1.1. Inject an 800-ppb single-component pesticide standard solution to prime (or deactivate) the column.

14.9.1.2. Run one or more solvent blanks consisting of hexane until no carryover is observed prior to analyzing any standards or samples.

14.9.2. Perform the following tasks to eliminate the degradation problem.

14.9.2.1. For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter.

14.9.2.2. Break off the first few centimeters (up to 30 cm) of the injection port side of the column.

14.9.2.3. Check the injector temperature and lower it to 205°C, if necessary.

14.9.2.4. Remove the columns and solvent backflush according to the manufacturer's instructions.

14.9.2.5. If all else fail, it may be necessary to deactivate the metal injector body and/or replace the columns.

14.9.3. Perform the following tasks to rinse the analytical column.

14.9.3.1. Depending on the nature of the residues expected, the first rinse might be reagent water, followed by methanol and acetone, with methylene chloride as the final rinse. In some cases, methylene chloride may be the only solvent necessary.

14.9.3.2. After the final rinse, the analytical column should be filled with methylene chloride and remained flooded overnight to allow materials within the stationary phase to migrate into the solvent.

14.9.3.3. The analytical column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

15. ▶CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peaks for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS.
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peaks for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample solvent extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. ►The target analyte concentration for a solid (***or*** oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (***or*** oil) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (***or*** oil) sample solvent extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a wipe (or filter) sample is calculated as follows:

$$C_W = C_{ex} \times V_{ex} \times D$$

where: C_W = concentration of target analyte in wipe (or filter) sample in µg/sample.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in L.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_{MP} = volume of mobility-procedure extract solvent extracted in mL. Unless specified otherwise, V_{MP} = 100.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.13. Refer to the preparatory method(s) for additional calculations.

15.14. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste samples, and µg/sample for wipe and filter samples.

15.14.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.15. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ►POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

18.4.1. For EPA Region 9 requirement, refer to Section 12.6.3.1.2. for acceptance criteria.

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil, and solid waste samples, and µg/sample for wipe and filter samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ▸CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, ***Quality Control Director,*** Quality Control Manager, Group Leader, and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ▸CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ▶REFERENCES

22.1. *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8082, USEPA, Revision 0, December 1996.

22.2. *Determinative Chromatographic Separations,* Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.3. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.7. *Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)*, SW-846 Method 8081 or 8080, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Quantitation Peaks for Multiple-Component Target Compounds.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8082 Revision 0 are noted.

Calscience SOP M407 Section	Reference Document EPA Method 8082 Section	Summary of Modification
All	All	None.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.0	Section 2: Add tissue matrix. Section 3: Update terminology for RL, and add reference to the determinations of DL and RL. Section 4: Revise the scope to indicate routine analytes. Section 5: Update method summary and EPA method numbers. Section 6: Delete internal standard definition. Add LOD and LOQ definitions. Section 7: Update interferences. Section 8: Update safety information. Section 9: Update the list of equipment and supplies. Section 10: Revise reagent and standard preparations. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Add calibration procedures. Section 14: Update procedures. Section 15: Add references to solvent extraction, mobility extraction, and tissue matrix. Section 18: Update section references, and add EPA Region 9 requirements.	J. Kang / K. Chang	01/28/13

Revision	Description	Author(s)	Effective Date
4.0	Section 22: Update references. Section 23: Update appendices. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Update Aroclor patterns. Appendix B: Update DoD quality control requirements and criteria.	J. Kang / K. Chang	01/28/13
5.1	Entire document: Update company name. Entire document: Remove tissue matrix. Section 5: Update method 3545 extraction solvent. Section 6: Update definitions. Sections 8 and 17: Add SDS. Section 9: Update equipment. Section 10: Add acetone/hexane. Sections 10, 12, 14, 18, and Appendix B: Update LCSD requirement. Sections 19 and 20: Update responsibilities.	L. Hunt	04/13/15

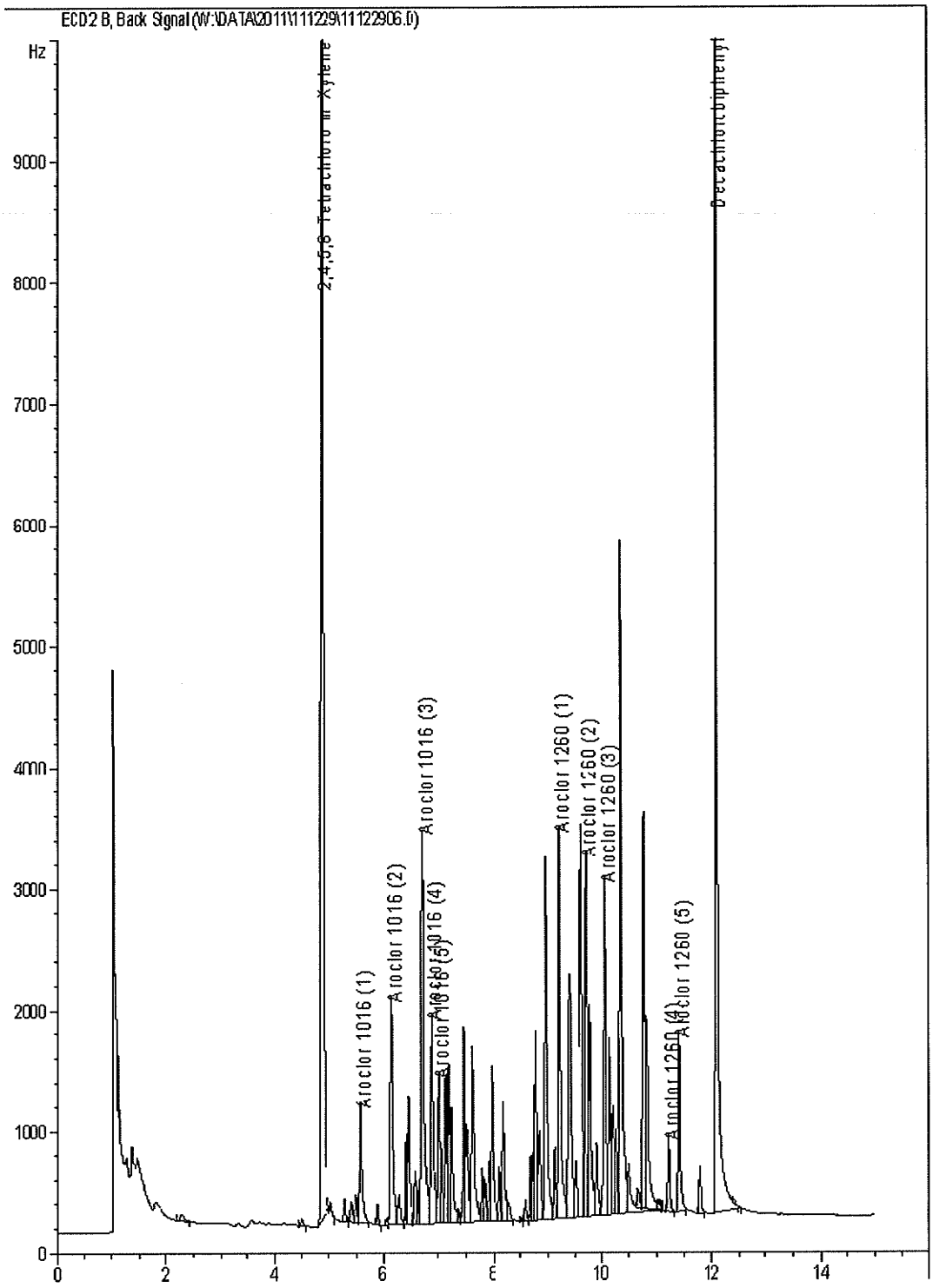
Appendix A

QUANTITATION PEAKS FOR MULTIPLE-COMPONENT TARGET COMPOUNDS

Eurofins Calscience, Inc.

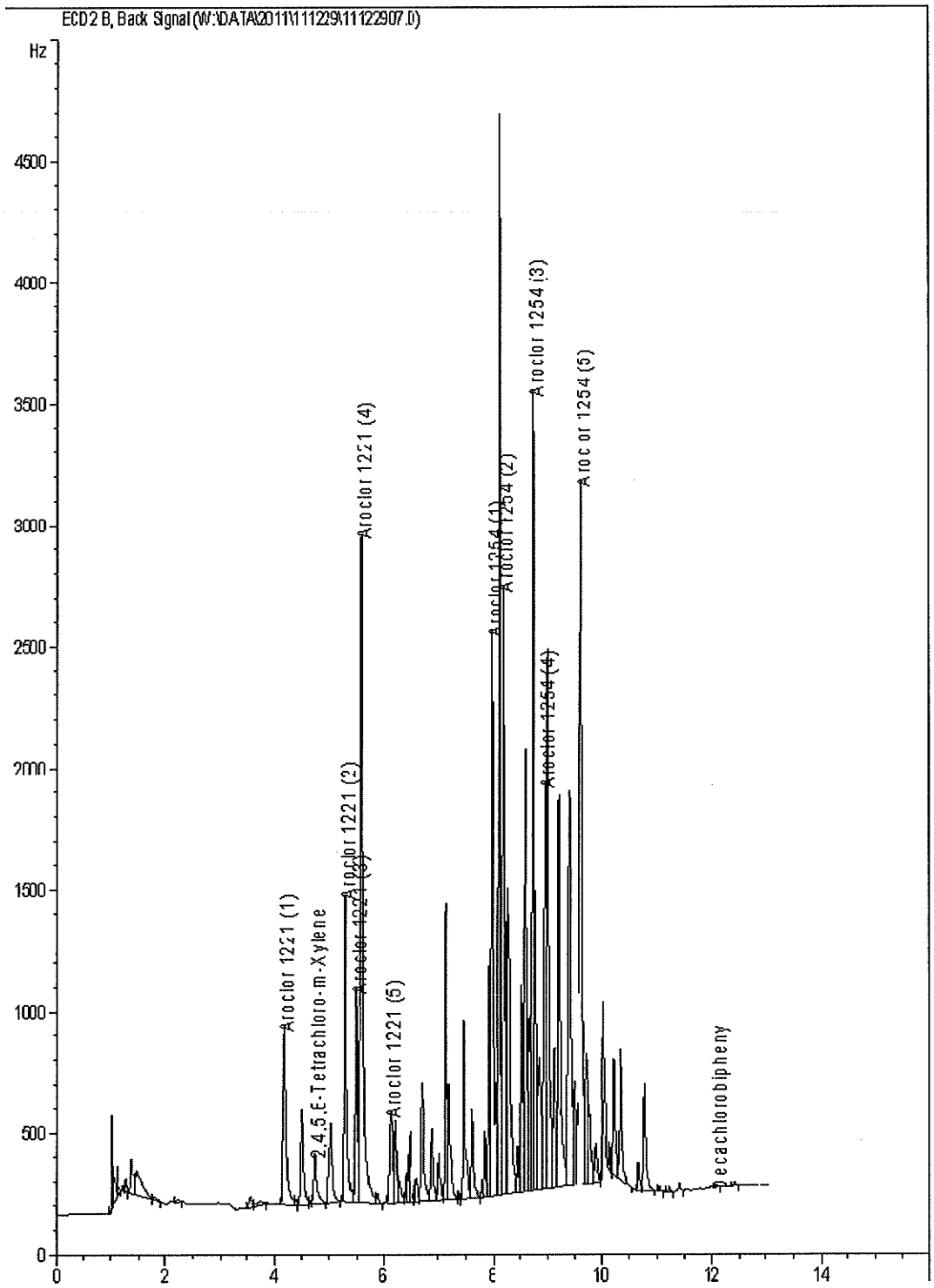
Appendix A

Quantitation Peaks for Aroclor 1016 and Aroclor 1260



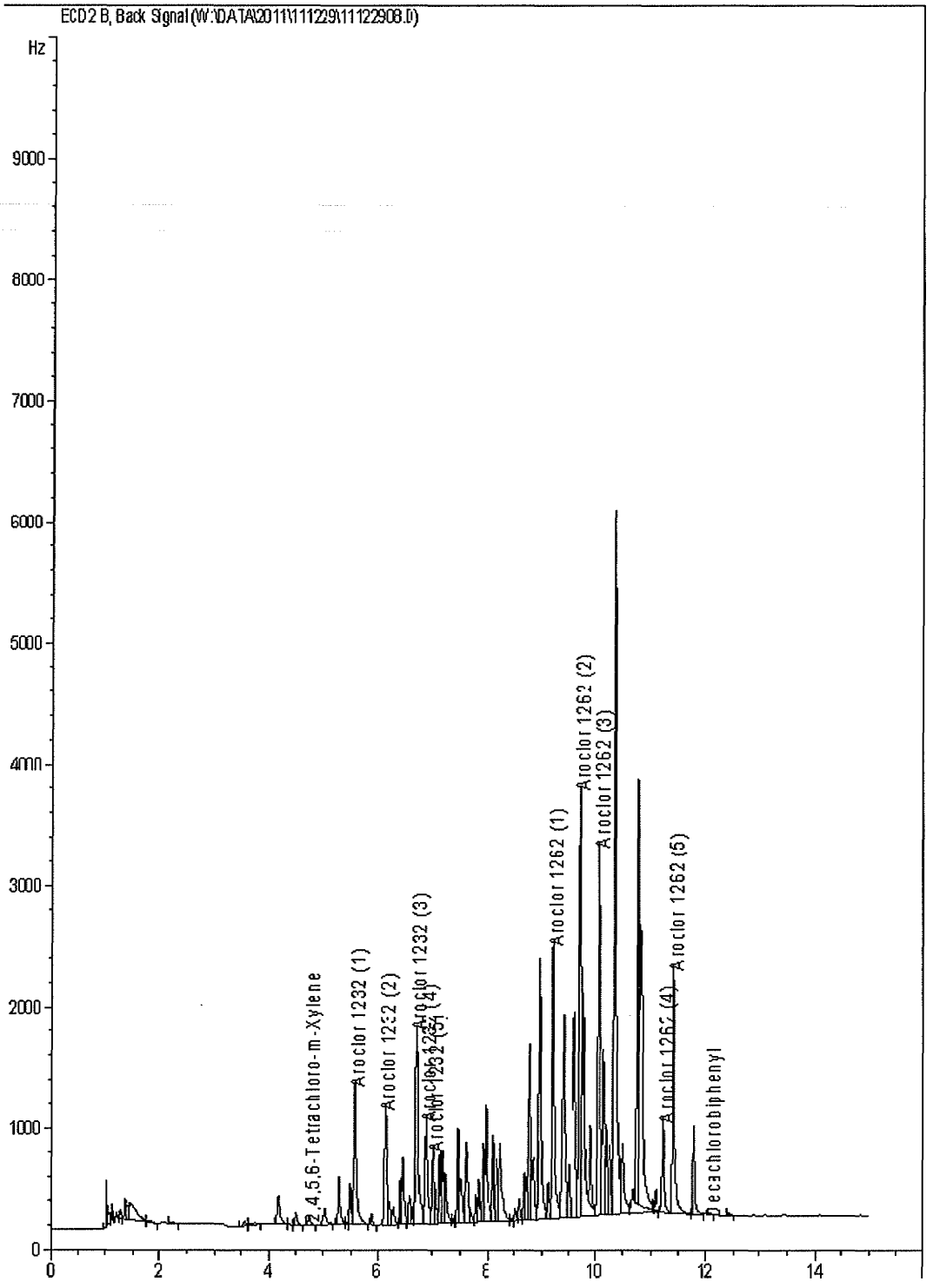
Appendix A

Quantitation Peaks for Aroclor 1221 and Aroclor 1254



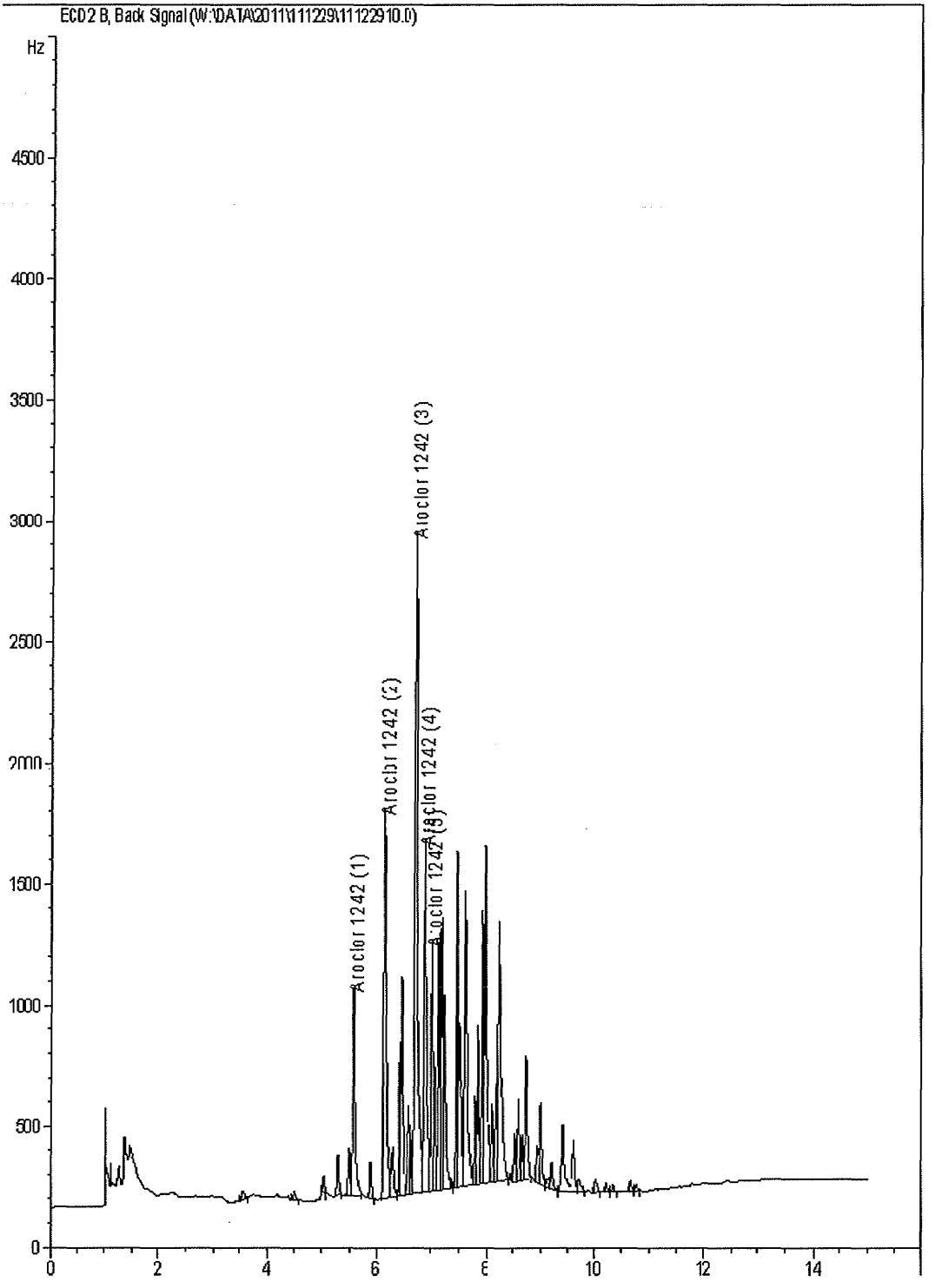
Appendix A

Quantitation Peaks for Aroclor 1232 and Aroclor 1262



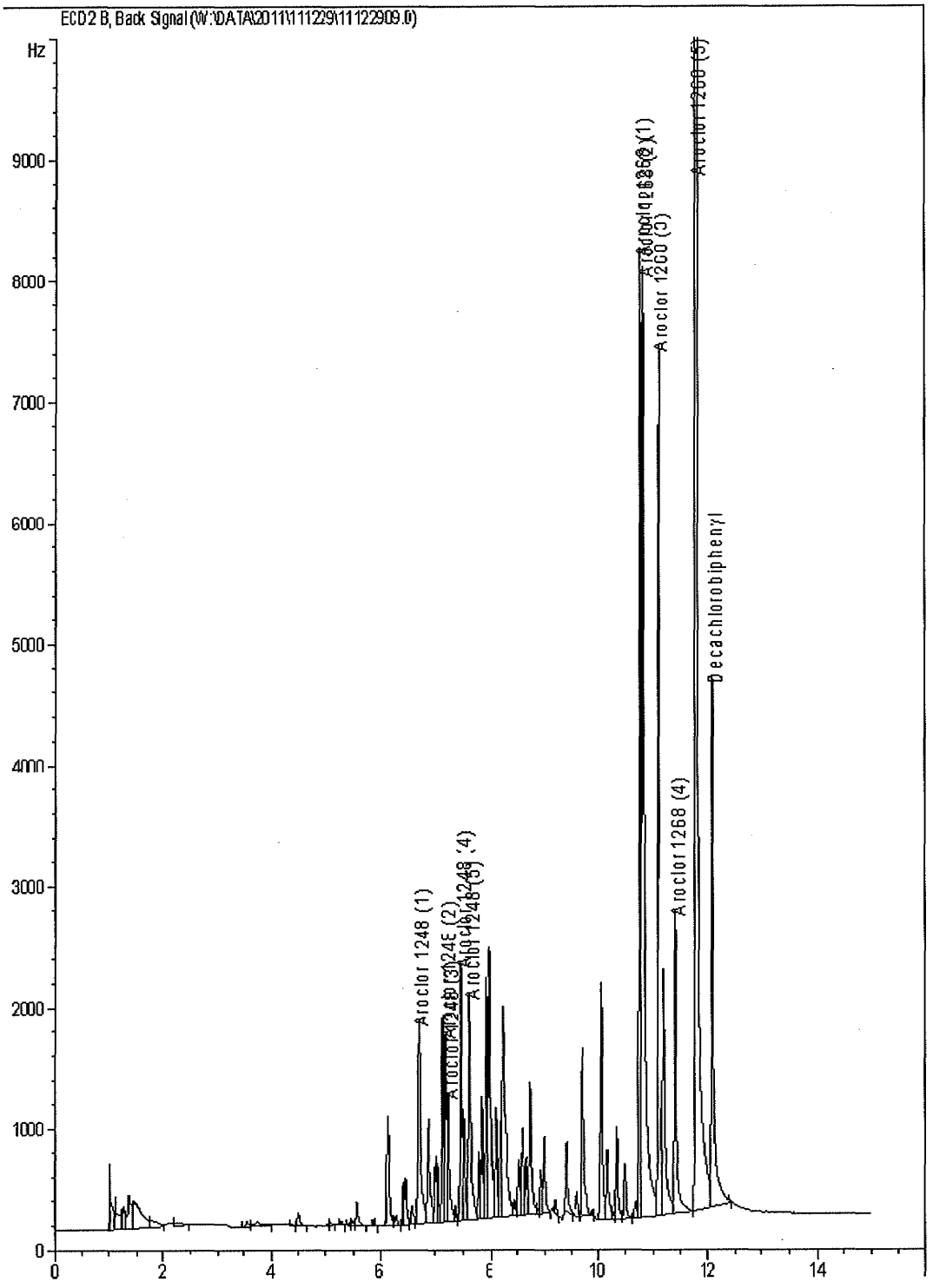
Appendix A

Quantitation Peaks for Aroclor 1242



Appendix A

Quantitation Peaks for Aroclor 1248 and Aroclor 1268



Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION / QUANTITATION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. ►STANDARDS

4.1. The spike standard solution shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The initial five-point calibration must be established for each Aroclor prior to the processing of sample extracts.

5.3.1.1. Results may not be quantitated using a single point.

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.4.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.5. Retention Time Window

5.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.5.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.5.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.6. Event Based Quality Control (MBs and LCSs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project-specific data quality objectives (DQOs).

5.6.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.6.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.6.2. Laboratory Control Samples (LCSs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed below.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.6.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.2.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.7.1. Surrogate

5.7.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed below.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Decachlorobiphenyl	40	135	60	125

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2. Matrix Spikes (MS/MSDs) and Surrogate

5.7.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed below. The RPD is ≤ 30%.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.7.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD-generated control limits shall be applied. If DoD-generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. ►PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

6.3.1.2. Follow project-specific reporting requirements when reporting data.

6.3.1.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

6.3.1.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

6.3.2. Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

Document No. : SOP-M311
Revision No. : 0.4
Supersedes : 0.3

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PROPRIETARY INFORMATION STATEMENT

Revision 0.4 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 3/16/2015
MANAGEMENT DATE

_____ 03/16/15
QA DEPARTMENT DATE

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable for ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Oil
VOCs	0.5~100 µg/L	5.0~250 µg/kg (wet-weight)	500~25000 µg/kg
Lower-QL VOCs	0.5~50.0 µg/L		

3.2. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8260B is used to determine the concentrations of most volatile organic compounds (VOCs) that have boiling points below 200°C and are insoluble or slightly soluble in water.

4.2. The following compounds are routinely determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol.

acetone*	chlorobenzene	1,2-dichloroethane
t-amyl methyl ether (TAME)	chloroethane	1,1-dichloroethene
benzene	chloroform	c-1,2-dichloroethene
bromobenzene	chloromethane*	t-1,2-dichloroethene
bromochloromethane	2-chlorotoluene	1,2-dichloropropane
bromodichloromethane	4-chlorotoluene	1,3-dichloropropane
bromoform	dibromochloromethane	2,2-dichloropropane
bromomethane*	1,2-dibromo-3-chloropropane*	1,1-dichloropropene
2-butanone*	1,2-dibromoethane (EDB)	c-1,3-dichloropropene
t-butyl alcohol (TBA)*	dibromomethane	t-1,3-dichloropropene
n-butylbenzene	1,2-dichlorobenzene	diisopropyl ether (DIPE)
s-butylbenzene	1,3-dichlorobenzene	ethanol*
t-butylbenzene	1,4-dichlorobenzene	ethylbenzene
carbon disulfide*	dichlorodifluoromethane*	ethyl t-butyl ether (ETBE)
carbon tetrachloride	1,1-dichloroethane	hexachloro-1,3-butadiene

2-hexanone*	1,1,1,2-tetrachloroethane	trichloroethene
isopropylbenzene	1,1,2,2-tetrachloroethane	trichlorofluoromethane
p-isopropyltoluene	tetrachloroethene	1,2,3-trichloropropane
methyl t-butyl ether (MTBE)	tetrahydrofuran	1,2,4-trimethylbenzene
methylene chloride	toluene	1,3,5-trimethylbenzene
4-methyl-2-pentanone (MIBK)*	1,2,3-trichlorobenzene	vinyl acetate
naphthalene	1,2,4-trichlorobenzene	vinyl chloride
n-propylbenzene	1,1,1-trichloroethane	o-xylene
styrene	1,1,2-trichloroethane	p/m-xylenes

4.3. The following compounds may also be determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol. Compounds requiring an unpreserved aqueous sample aliquot for analysis are denoted with the "**" symbol.

acetonitrile*	hexane
acrolein*	iodomethane
acrylonitrile*	isobutyl alcohol*
allyl chloride	isopropanol*
1,3-butadiene	methacrylonitrile*
2-chloroethyl vinyl ether**	methyl acetate
chloroprene	methyl methacrylate
1-chloropropane	2-methyl-2-butanone (TAA)
2-chloropropane	methylcyclohexane
cyclohexane	propanedinitrile
cyclohexanone	propionitrile
t-1,4-dichloro-2-butene*	thiophene
diethyl ether	1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
1,4-dioxane*	2,2,4-trimethyl pentane
ethyl methacrylate	

4.4. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8260B determination, either by regulatory reference or validation studies.

4.5. Most volatile organic compounds may be introduced into the GC/MS system via purge-and-trap method (EPA Method 5030) and closed system purge-and-trap method (EPA Method 5035).

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph / mass spectrometer (GC/MS) and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. EPA Method 8260B describes chromatographic procedures that will allow for the separation of volatile organic compounds and their qualitative and quantitative analysis by gas chromatography and mass spectrometry. Detection is achieved using a mass selective detector (MSD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Volatile organic compounds in a sample are introduced into the gas chromatograph via the appropriate purge-and-trap method. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Purge-and-Trap for Samples	5030	SOP-M212
Closed System Purge-and-Trap for Soil/Waste Samples	5035	SOP-M213
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

5.4. Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator. Identification of target analytes is accomplished by comparing their mass spectra with the mass spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.28. Term Specific to GC/MS Analysis

6.28.1. Mass-to-Charge Ratio (m/z): The dimensionless quantity formed by dividing the mass of an ion in unified atomic mass units by its charge number (regardless of sign).

6.29. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Samples can become contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage.

7.1.1. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination. Refer to the current revision of SOP-T011, "Field QA/QC Samples" for guidance.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.3. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The laboratory where the analysis is to be performed should be free of solvents other than water and methanol.

7.3.1. Many common solvents, most notably acetone and methylene chloride, are frequently found in the laboratory air at low levels. The sample receiving chamber should be loaded in an environment that is clean enough to eliminate the potential for contamination from ambient sources.

7.4. The use of non-polytetrafluoroethylene (non-PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation.

7.4.1. Analyses of reagent blanks provide information about the presence of contaminants. However, subtracting blank values from sample results is not permitted.

7.5. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially.

7.5.1. Sample syringe and/or purging device should be thoroughly rinsed with organic-free reagent water between samples.

7.5.2. Analysis of a suspected high level sample should be followed by an analysis of organic-free reagent water to check for cross-contamination.

7.5.3. For volatile samples containing high concentrations of water-soluble materials, suspended solids, or high boiling-point compounds, it may be necessary to clean purging device, rinse it with organic-free reagent water, and then dry in an oven at 105°C between analyses.

7.6. If elevated baselines are observed during the analysis of blanks and standards, the chromatographic system should be considered contaminated. This contamination may be the result of impure carrier gas, inadequate gas conditioning, septum bleed, column oxidation, and/or pyrolysis products in the injector or column. Such contamination is unacceptable and should be addressed through a program of preventive maintenance and corrective action.

7.7. Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing.

7.8. Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

7.9. Co-elution of the p- and m-xylene isomers may occur.

7.10. Refer to the preparatory method for other potential interferences.

8. ►SAFETY

8.1. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzene, bromodichloromethane, bromoform, carbon tetrachloride, chloroform, dibromochloromethane, 1,4-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, methylene chloride, 1,1,2,2-tetrachloroethane, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA-approved-toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

8.4. Refer to the preparatory methods for additional safety issues.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890 Series Gas Chromatograph, Agilent 6890N Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components:

9.1.1. Purge-and-trap system (see the appropriate preparatory method).

9.2. Mass Spectrometer: Agilent 5973Network Mass Selective Detector (MSD), Agilent 5975B MSD, Agilent 5975C MSD, or equivalent capable of scanning from 35 to 270 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron-impact ionization (EI) mode, and configured with the following components:

9.2.1. Electron-ionization ion source.

9.2.2. Hyperbolic quadrupole mass filter.

9.2.3. High energy dynode (HED) electron multiplier (EM) detector.

9.3. Instrument Software

9.3.1. Requires a PC-based data system or equivalent.

9.3.2. Agilent MSD ChemStation Version E.02.00.493, Agilent MSD ChemStation Version E.02.01.1177, or equivalent equipped with NIST mass spectral library.

9.4. Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 and instrument manuals for maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 25-m × 0.2-mm ID, 1.12-µm film thickness, mid-polar, low bleed, narrow-bore, capillary, fused silica, J&W Scientific DB-624 or equivalent.

9.6. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.7. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.8. VOA vials, 28-mm × 95-mm (40 mL capacity) and 28-mm × 57-mm (20-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.8.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.9. Storage vials, 15-mm × 45-mm (4 mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.10. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.11. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.13. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 100 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 1 L with additional reagent water.

10.1.5. Hydrochloric acid, HCl, 36.5−38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.6. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.6.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.7. Sodium bisulfate, $NaHSO_4$, monohydrate, colorless crystals, reagent grade or equivalent.

10.1.8. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. ►Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each gaseous volatile organic target analyte are used to prepare calibration and check standards.

10.2.1.1. The gaseous target analytes are dichlorodifluoromethane (CFC-12), chloromethane (methyl chloride), vinyl chloride, bromomethane (methyl bromide), chloroethane (ethyl chloride), and trichlorofluoromethane (CFC-11).

10.2.1.2. Prepare each 50 ppm gaseous volatile organic working standard solution by diluting 1.25 mL of the 2000 ppm gaseous volatile organic stock standard to 50.0 mL with methanol.

10.2.1.3. The 50 ppm gaseous volatile organic working standard solutions must be stored under dark and refrigerated conditions, and replaced after two weeks or sooner if comparison with check standards indicates a problem.

10.2.2. ***Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000–20000 ppm of various (custom and catalogued mixes) of non-gaseous volatile organic target analytes are used to prepare calibration and check standards.***

10.2.2.1. ***Use following table as guidance to prepare the primary source working standard in methanol.***

VENDOR	CAT #	Description	Conc. PPM	uls	MLs	PPM
ACCU	S-21698-R7	CUSTOM VOC STANDARD	2000-20000	1000	40	50-500
CHEMSERV.	From NEAT	ACROLEIN	10000	400	40	50-500
RESTEK	30216	VINYL ACETATE	2000	1000	40	50-500
RESTEK	30265	2-CHLOROETHYL VINYL ETHER	2000	1000	40	50-500
RESTEK	30465	CALIFORNIA OXYGENATES MIX # 1	2000-10000	1000	40	50-500
RESTEK	30633	8260B CALIBRATION MIX # 1	2000	1000	40	50-500
RESTEK	30006	VOA CALIBRATION MIX # 1	5000	400	40	50-500

10.2.2.2. ***Prepare the 0.5–5.0 ppm gaseous and non-gaseous volatile organic working standard solution by diluting the appropriate volume of 50-500 ppm gaseous and non-gaseous volatile organic stock standard to 1.0 mL with methanol.***

10.2.2.3. ***The 0.5-5.0 ppm volatile organic working standard solution must be prepared fresh on the day of calibration.***

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing ***12500*** ppm of each surrogate, ***12500*** ppm of each internal standard (except TBA-d_9), and ***62500*** ppm of TBA-d_9 are used to prepare surrogate and internal standard working standards.

10.2.3.1. The surrogates are 1,4-bromofluorobenzene (BFB), dibromofluoromethane, 1,2-dichloroethane-d_4, and toluene-d_8.

10.2.3.2. The internal standards are t-butyl alcohol-d_9 (TBA-d_9), chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, 1,4-difluorobenzene, and pentafluorobenzene.

10.2.3.2.1. The internal standards selected should permit most analytes of interest in a chromatogram to have relative retention times of 0.80–1.20.

10.2.3.3. Prepare the 50 ppm and 250 ppm surrogate and internal standard working standard solutions by diluting the appropriate volumes of the surrogate and internal standard stock standards to 50 mL with methanol.

10.2.3.4. The 50 ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	2500	1.0	50	50
dibromofluoromethane	2500		50	
1,2-dichloroethane-d_4	2500		50	
toluene-d_8	2500		50	
TBA-d_9	12500	1.0	250	
chlorobenzene-d_5	2500		50	
1,4-dichlorobenzene-d_4	2500		50	
1,4-difluorobenzene	2500		50	
pentafluorobenzene	2500		50	

10.2.3.5. The 250 ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	12500	1.0	250	50
dibromofluoromethane	12500		250	
1,2-dichloroethane-d_4	12500		250	
toluene-d_8	12500		250	
TBA-d_9	62500	1.0	1250	
chlorobenzene-d_5	12500		250	
1,4-dichlorobenzene-d_4	12500		250	
1,4-difluorobenzene	12500		250	
pentafluorobenzene	12500		250	

10.2.3.6. Prepare the first calibration standard or CCV solution, and purge and trap for hardware turning.

10.2.4. Calibration standard solutions contain various concentrations of target analytes, surrogates, and internal standards in methanol.

10.2.4.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the ***50/***250 ***or 250/1250*** ppm ***(as per autosampler)*** surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration.

10.2.4.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50***/250*** ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.4.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.4.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	50	0.5~5.0	250	5.0	1.0
1.0	2.0	5.0	10	50	0.5~5.0	250	10.0	1.0
10	20	50	100	50	50~500	250	1.0	1.0
20	40	100	200	50	50~500	250	2.0	1.0
50	100	250	500	50	50~500	250	5.0	1.0
100	200	500	1000	50	50~500	250	10.0	1.0
200	400	1000	2000	50	50~500	250	20.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 250 ppb;
Initial Concentration of TBA-d_9 = 1250 ppm

10.2.4.3. Use the following calibration levels as guidance to prepare the calibration standards for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	10	0.5~5.0	50	20.0	4.0
2.0	4.0	10	20	10	0.5~5.0	50	80.0	4.0
5.0	10	25	50	10	50~500	50	2.0	4.0
10	20	50	100	10	50~500	50	4.0	4.0
20	40	100	200	10	50~500	50	8.0	4.0
30	60	150	300	10	50~500	50	12.0	4.0
40	80	200	400	10	50~500	50	16.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 50 ppb; Initial Concentration of TBA-d_9 = 250 ppm

10.2.4.4. The midpoint standards are also used as the continuing calibration verification solutions.

10.2.4.5. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.5. Initial calibration verification (ICV) solutions contain the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.1. Add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 250 ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration verification.

10.2.5.1.1. For lower limit of quantitation, add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 50 ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.5.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.5.2. Use the following calibration level as guidance to prepare the ICV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 250 ppb;
Initial Concentration of TBA-d_9 = 1250 ppm

10.2.5.3. Use the following calibration level as guidance to prepare the ICV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 50 ppb;
Initial Concentration of TBA-d_9 = 250 ppm

10.2.5.4. The calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.6. Continuing calibration verification (CCV) solutions contain the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.6.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the 250 ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for continuing calibration verification.

10.2.6.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50 ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.6.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.6.2. Use the following calibration level as guidance to prepare the CCV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol*; A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 250 ppb; Initial Concentration of TBA-d_9 = 1250 ppm

10.2.6.3. Use the following calibration level as guidance to prepare the CCV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate; IS = Internal Standard; A = A1 + A2 + A3 + A4; Calibration Level of TBA-d_9 = 50 ppb; Initial Concentration of TBA-d_9 = 250 ppm

10.2.6.4. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.7. Surrogate and internal standard working standard solutions contain 50/250 ppm of each surrogate, 50/250 ppm of each internal standard (except TBA-d_9), and 250/1250 ppm of TBA-d_9 in methanol.

10.2.7.1. If autosampler is <u>not</u> capable of injecting standard solution automatically, manually add 5.0 µL of the 50 ppm surrogate and internal standard working standard to each sample including each calibration standard, calibration verification standard, quality control (QC) check sample, and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.1.1. For lower limit of quantitation, manually add 4.0 µL of the 50 ppm surrogate and internal standard working standard to each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20 mL purge volume.

10.2.7.1.2. For samples processed via mobility or methanol extraction, manually add 5.0 µL of the 50 ppm

surrogate and internal standard working standard to each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.2. If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the 250 ppm surrogate and internal standard working standard into each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.2.1. For lower limit of quantitation, configure the autosampler to inject 4.0 µL of the 50 ppm surrogate and internal standard working standard into each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20 mL purge volume.

10.2.7.2.2. For samples processed via mobility or methanol extraction, configure the autosampler to inject 1.0 µL of the 250 ppm surrogate and internal standard working standard into each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.8. Spike working standard solutions contain various concentrations of target analytes in methanol. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. Use the second source 50 ppm gaseous volatile organic working standard solution as the gaseous spike working standard solution. Use the second source non-gaseous volatile organic stock standard solution as the non-gaseous spike working standard solution.

10.2.8.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

10.2.8.3. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS sample prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.8.3.1. For lower limit of quantitation, add 4.0 µL of the gaseous spike working standard and 4.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS sample prior to purge-and-trap extraction via 20 mL purge volume.

10.2.8.4. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each mobility-procedure or methanol extract designated as MS/MSD and LCS prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.9. All working standards must be replaced after three months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.9.1. Store all working standards with minimal headspace under dark and refrigerated condition.

10.2.9.2. Return the working standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.9.3. Check all working standards frequently for signs of degradation or evaporation.

10.2.10. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.10.1. Return the stock standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.10.2. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40 mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. Collect all samples in triplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, collect the sample in a 125 mL amber glass container containing 4 drops of the 10% $Na_2S_2O_3$ solution. Gently swirl to mix the sample, and transfer to pre-cleaned amber glass or clear glass VOA vials.

11.1.1.1. Aqueous sample containing greater than 5 mg/L of residual chlorine may require additional amount of the dechlorinating agent.

11.1.2. Adjust the pH of the aqueous sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.2.1. If a dechlorinating agent and acid are both added as preservatives, the aqueous sample must be dechlorinated first and then acidified.

11.1.2.2. Reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, and vinyl chloride) are unstable at low pH. It is recommended that a second set of the aqueous sample without acid preservative be collected.

11.1.2.3. If fuel oxygenated compounds are the only analytes of interest, and the aqueous sample will be purged at an elevated temperature of 80°C, no acid preservation is required.

11.1.2.4. If carbonaceous materials are present, the aqueous sample should not be acid preserved due to possible effervescence and loss of volatile organic compounds.

11.1.2.5. If aromatic and biologically active compounds are the analytes of interest, acid preservation is necessary.

11.1.3. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.1.4. A reagent water trip blank, preserved in the same manner as the field samples, should accompany each batch of aqueous samples.

11.2. Solid samples for EPA Method 5030 purge-and-trap extraction should be collected in 4 oz or 8 oz pre-cleaned clear glass wide-mouth jars, or 6 in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.2.1. A reagent water trip blank should accompany each batch of solid samples.

11.3. Solid samples for EPA Method 5035 closed system purge-and-trap extraction should be collected in Terra Core Samplers, En Core® Samplers, or equivalent. Collect all samples in triplicate.

11.3.1. Solid samples collected using the Terra Core or equivalent coring device shall be immediately extruded into a pre-weighed 40 mL amber glass or clear glass VOA vial containing 5 mL of sodium bisulfate solution and a magnetic stirring bar, or 10 mL of methanol, and sealed with a Teflon-lined septum and screw cap by client field personnel.

11.3.2. If sample result is to be reported on a dry weight basis, one additional solid sample should be collected in a 4 oz pre-cleaned clear glass wide-mouth jar with a Teflon-lined closure, and labeled specifically for solids content determination.

11.3.3. If MS/MSD analyses are required, collect one sample in quintuplicate.

11.3.4. A reagent water trip blank should accompany each batch of solid samples.

11.4. Oil samples should be collected in 40 mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.4.1. A reagent water trip blank should accompany each batch of oil samples.

11.5. Mobility-procedure extracts should be collected in 20 mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.5.1. If the mobility-procedure extract will not be analyzed within 24 hours, collect the mobility-procedure extract in a 40 mL pre-cleaned amber glass or clear glass VOA vial, and adjust the pH to < 2 by adding 1:1 HCl solution while stirring.

11.5.1.1. If effervescence (bubbling, hissing, or foaming of liquid as gas escapes) is observed upon adding 1:1 HCl solution, do not acid preserve the mobility-procedure extract.

11.5.2. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.5.2.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.6. Aqueous and oil samples should be maintained in a chilled state (0–6°C), not frozen, post sample collection until received at the laboratory. If shipped on same day as collection, sediment samples should be maintained in a chilled state, 0–6°C, post sample collection. Otherwise freeze sediment samples as soon as possible after collection and maintain them at ≤ -10°C until shipment. Solid samples may be frozen if solids content determination is not required. Freezing of solid samples may require contract approval.

11.6.1. Freezing solid samples within 48 hours of sample collection can minimize biodegradation of aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes).

11.7. Upon receipt, the aqueous, oil, and unfrozen solid samples are stored in a 0–6°C cooler. Sediment samples are stored in a ≤ -10°C freezer. Solid samples may be stored in a ≤ -10°C freezer if solids content determination is not required.

11.7.1. Aqueous samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.7.2. Aqueous samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

11.7.2.1. Aqueous samples containing highly reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, vinyl chloride, etc.) as target analytes should be analyzed as soon as possible.

11.7.3. Solid samples collected in jars or sleeves must be analyzed within 14 days of sample collection.

11.7.4. High concentration (> 200 µg/kg) solid samples collected in jars or sleeves must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.4.1. Methanol extracts shall be stored in a 0–6°C cooler. Per client request or project specific data quality objectives (DQOs), apply the specified minimum contact time between the solid sample and methanol prior to analysis.

11.7.5. Solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with sodium bisulfate solution and analyzed within 14 days of sample collection.

11.7.5.1. Solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.5.2. Solid samples may also be analyzed within 48 hours of sample collection without sodium bisulfate preservation.

11.7.6. High concentration (> 200 µg/kg) solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.6.1. High concentration solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.6.2. Methanol extracts shall be stored in a 0–6°C cooler. Per client request or project specific DQOs, apply the specified minimum contact time between the solid sample and methanol prior to analysis.

11.7.7. Oil samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.7.1. Methanol extracts shall be stored in a 0–6°C cooler. Per client request or project specific DQOs, apply the specified minimum contact time between the solid sample and methanol prior to analysis.

11.7.8. Mobility-procedure extracts with acid preservation (pH < 2) must be analyzed within 14 days post mobility extraction for aqueous samples, or within 7 days post mobility extraction for solid samples.

11.7.8.1. Mobility-procedure extracts shall be stored in a 0–6°C cooler post mobility extraction if analysis is not to be performed within 24 hours.

11.7.9. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be analyzed within 24 hours post mobility extraction.

11.7.10. Storage blanks consisting of clean reagent water should be used to monitor potential cross-contamination of samples due to improper storage conditions.

12. ▶QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the defined acceptance criteria.

12.1.2. The following criteria must be demonstrated every 12 hours.

m/z	Relative Abundance Criteria
50	15 – 40% of m/z 95
75	30 – 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 – 9% of m/z 95
173	< 2% of m/z 174
174	> 50% of m/z 95
175	5 – 9% of m/z 174
176	> 95% but < 101% of m/z 174
177	5 – 9% of m/z 176

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action and re-tune the system.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of samples.

12.2.1.1. The calibration curve is established with a minimum of five calibration standards, but may contain six or seven calibration standards.

12.2.2. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average relative response factor (RRF) for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.2.2.1. The calibration check compounds (CCCs) are chloroform, ethylbenzene, 1,1-dichloroethene, 1,2-dichloropropane, toluene, and vinyl chloride.

12.2.2.2. The system performance check compounds (SPCCs) are bromoform, chlorobenzene, chloromethane, 1,1-dichloroethane, and 1,1,2,2-tetrachloroethane.

12.2.3. If the %RSD for an analyte is ≤ 15%, the RRF is assumed to be constant over the calibration range, and the average RRF may be used for quantitation.

12.2.4. In those instances where the %RSD for one or more target analytes exceeds 15%, the initial calibration remains acceptable if the mean of the %RSD values for all analytes in the calibration is ≤ 15%. This approach (i.e., the average of all %RSD values ≤ 15%) is referred to as the grand mean approach. The grand mean approach cannot be used for Department of Defense projects.

12.2.4.1. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.1.1. The mean %RSD criterion applies to all analytes in the calibration standards, regardless of whether or not they are of interest for a specific project. In other words, if the analyte is part of the calibration standard, its %RSD value is included in the evaluation.

12.2.4.2. If the grand mean approach is utilized, the average RRF with %RSD > 15% may be used for quantitation.

12.2.4.2.1. Per client request or project specific data quality objectives (DQOs), a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded 15%, and the results of the mean %RSD calculation must be included in the data package.

12.2.4.3. The use of the grand mean approach will lead to greater uncertainty for those analytes for which the %RSD is > 15%. Review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results, to determine if the calibration linearity poses a significant concern.

12.2.4.3.1. If the grand mean approach is not acceptable due to client or project specific requirements (such as Department of Defense project criteria), employ one of the other calibration options (see Section 12.2.5.), or adjust instrument operating conditions and/or the calibration range until the %RSD is ≤ 15%.

12.2.5. Other calibration options are as follows:

12.2.5.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.99.

12.2.5.2. The section calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

12.2.5.2.1. This option requires at least six calibration levels.

12.2.6. The relative retention time (RRT) of each analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.7. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.7.1. If the RSD or correlation of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.2.7.2. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis to rule out problems due to random chance.

12.2.7.2.1. In some cases, replace the calibration standard may be necessary.

12.2.7.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD or correlation, and document the rationale for re-analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.3.1.1. If the calibration option is average relative response, the %D is the percent difference.

12.3.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.3.2. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.3.3. The internal standard response and retention time for the ICV must be evaluated during or immediately after data acquisition.

12.3.3.1. If the extracted ion current profile (EICP) area of any internal standard in an ICV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.3.3.2. If the retention time of any internal standard in an ICV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.3.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.4.2.1. If the calibration option is average relative response, the %D is the percent difference.

12.4.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.4.2.3. For EPA Region 9 requirement, the initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.3. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.4.4. The internal standard response and retention time for the CCV must be evaluated during or immediately after data acquisition.

12.4.4.1. If the EICP area of any internal standard in a CCV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.4.4.2. If the retention time of any internal standard in a CCV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.4.4.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

12.4.5. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Event Based Quality Control (MBs and LCSs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB) and a laboratory control sample and laboratory control sample duplicate (LCS).

12.5.1.1. An LCS shall be prepared whenever there is insufficient sample volume to perform the needed matrix QC (duplicate or MS/MSD) or as required by project QAPP. In all other instances a single LCS shall be prepared.

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.5.2.2. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source

of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

12.5.3. ►The acceptance criteria for LCS compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC and RPD ***(if applicable)*** of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS compound are 80% and 120%, respectively. The RPD ***(between LCS and LCSD)*** is ≤ 20%.

12.5.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS compound in a water sample are 70% and 130%, respectively. The RPD is ≤ 30%.

12.5.3.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS compound in a soil sample are 65% and 135%, respectively. The RPD is ≤ 50%.

12.5.3.2. All LCS compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Lower and upper marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.3.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.3.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.3.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 - 90	4
51 - 70	3
31 - 50	2
11 - 30	1
< 11	0

12.5.3.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), and surrogates and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate compounds are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each surrogate compound are 70% and 130%, respectively.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound in a water sample are 85% and 115%, respectively.

12.6.2.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound in a soil sample are 70% and 125%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. Unacceptable surrogate recoveries do not automatically invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same sample should be re-processed and re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

12.6.2.4.3.1. If, upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-processed and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for internal standard compounds are as follows:

12.6.3.1. It is recommended that the internal standard responses (area counts) and retention times for each standard, sample, and blank be monitored for method performance, injection execution, system/instrument maintenance, analytical errors, or interferences.

12.6.3.2. The area count of each internal standard peak in a standard, sample, or blank should be within 50% to 200% of that in the midpoint calibration standard for the most recent initial calibration.

12.6.3.3. The retention time of each internal standard peak in a standard, sample, or blank should be within ± 30 seconds of that in the midpoint calibration standard for the most recent initial calibration.

12.6.4. The acceptance criteria for MS/MSD compounds are as follows:

12.6.4.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.4.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD compound are 70% and 130%, respectively. The RPD is ≤ 30%.

12.6.4.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a water sample are 65% and 135%, respectively. The RPD is ≤ 30%.

12.6.4.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a soil sample are 50% and 150%, respectively. The RPD is ≤ 50%.

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS. Specifically, an acceptable LCS usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Mass Spectrometer Tuning

13.1.1. Prior to initial calibration and the analysis of field or QC samples, the GC/MS system must be hardware tuned such that the analysis of 5−50 ng of BFB meets the tuning criteria. The acceptance criteria for the tune are listed in Section 12.1.

13.1.2. Obtain the mass spectrum of BFB as follows:

13.1.2.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of BFB.

13.1.2.1.1. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

13.1.2.1.2. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

13.1.3. All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.

13.1.4. Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.

13.2. Mass Spectrometer Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.1.1. Recalibration is required for the following maintenance procedures.

13.2.1.1.1. Change, replace, or reverse the analytical column.

13.2.1.1.2. Replace the trap on a purge-and-trap system.

13.2.1.1.3. Change the entrance lens, draw-out lens, or repeller.

13.2.1.1.4. Change the electron multiplier and/or ion source chamber.

13.2.1.1.5. Clean the ion source and/or quadrupole rods.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. ▶PROCEDURE

14.1. Instrument Setup

14.1.1. Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.

14.1.2. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Mode	split
Split ratio	100 : 1
Split flow rate	48.9 mL/min
Inlet pressure	7.41 psi
Total flow rate	52.5 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to 190°C at 12.00°C/min 190°C, hold 0.50 min 190°C to 230°C at 45.00°C/min
Final temperature	230°C, hold 3.11 min
Transfer line temperature	260°C
Scan range	35~270 amu
Detector threshold	150

14.1.3. The sampling rate shall result in at least five full mass spectra across the chromatographic peak, and within 1 second or less per mass spectrum.

14.1.4. Once established, the same operating conditions must be applied to all subsequent standard, sample, and blank analyses.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4.

14.2.1. If a CCV fails, effect corrective action prior to analyzing any samples.

14.3. Following purge-and-trap preparation by the method specified in Section 5.2., the QC and actual environmental samples are received in purge vessels. The purge vessels are then loaded onto the purge-and-trap system.

14.4. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)–***Optional***
4) Method Blank (MB)
5) Samples (up to 20 per batch, excluding QC check samples and MBs)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance, and a CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. A tune meeting the acceptance criteria and an acceptable CCV are required daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

14.4.1.1. The tuning standard is also the CCV solution.

14.4.2. Item 2: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand. For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS. For methanol extracts, the LCS consists of the specified compounds spiked into the methanol extract designated as LCS.

14.4.2.2. One LCS is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8. The LCSD is required if MS/MSD are not prepared and analyzed along with field samples.

14.4.4. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

14.4.4.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB. For methanol extracts, the MB consists of the methanol extract designated as MB.

14.4.4.2. One MB is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5. ►Item 5: Up to 20 samples (excluding QC check samples and method blanks) per batch. High concentration samples should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.5.1. ***NOTE: For prescreening water samples of unknown concentration using portable PID detector, use the following precautions:***

14.4.5.1.1. First take a 5 mL aliquot of water sample from the vial using syringe and set aside.

14.4.5.1.2. Use rest of the vial for PID screening so that sample aliquot is uncompromised and sustains no loss of analytes.

14.4.5.1.3. Use the 5 mL aliquot for necessary dilution or run without dilution as determined by PID reading.

14.4.5.2. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.6. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.6.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.7.

14.4.6.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.7. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8.

14.4.8. Solvent blanks consisting of reagent water may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration samples), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of the appropriate surrogate and internal standard working standard solution is present in the autosampler standard vial(s) if the

autosampler is configured to inject standard solution automatically, and that a sufficient unused volume exists in the autosampler waste containers at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the response (area count) and retention time of each internal standard compound in each standard, sample, and blank (see Section 12.6.3.).

14.8.2. Qualitative identification of each analyte/surrogate is based on retention time of the sample component, and on comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

14.8.2.1. The reference mass spectrum must be generated using the same conditions of this method.

14.8.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.2.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte.

14.8.2.3.1. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

14.8.3. Target analytes are identified as present when the following criteria are met.

14.8.3.1. The intensities of the characteristic ions of an analyte maximize in the same scan or within one scan of each other.

14.8.3.1.1. Selection of a peak by a data system target analyte search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at an analyte-specific retention time will be accepted as meeting this criterion.

14.8.3.2. The RRT of the sample analyte is within ± 0.06 RRT units of the RRT of the standard analyte.

14.8.3.3. The relative intensities of the characteristic ions in the sample spectrum agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.8.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

14.8.3.4.1. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.3.5. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of analytes.

14.8.3.5.1. When analytes coelute, the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting analyte.

14.8.4. Tentative identification of a non-target analyte can be accomplished by using the data system library search. Refer to SOP-T025 for procedure.

14.8.4.1. The search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

14.8.4.2. The guidelines for making tentative identifications are as follows:

14.8.4.2.1. Relative intensities of major ions (ions greater than 10% of the most abundant ion) in the reference spectrum should be present in the sample spectrum.

14.8.4.2.2. Relative intensities of major ions in the sample spectrum should agree within ± 20% of those in the reference spectrum.

14.8.4.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

14.8.4.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting analytes.

14.8.4.2.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from sample spectrum due to background contamination or coeluting analytes.

Data system library reduction program can sometimes create these discrepancies.

14.8.5. Quantitation of a target analyte is based on the integrated abundance from the EICP of the primary characteristic ion.

14.8.5.1. Proper quantitation requires the appropriate selection of a baseline and integration from which the area of the characteristic ion peak can be determined.

14.8.5.2. Determine the concentration based on the initial calibration curve.

14.8.5.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RRFs, the area of the characteristic ion peak, and the internal standard concentration and ion peak area. The formula for calculating concentration is listed in Section 15.9.

14.8.5.2.2. The data system is programmed to perform the calculation of concentration.

14.8.5.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze.

14.8.5.4. For any non-target analyte identified in a sample extract, estimate the concentration as follows:

14.8.5.4.1. Obtain the area of the characteristic ion peak for the non-target analyte and the internal standard ion peak area from the total ion chromatogram.

14.8.5.4.2. Assume the average of the initial RRFs for the non-target analyte to be 1.

14.8.5.4.3. Calculate and report the concentration as an estimated value.

14.8.6. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.6.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.6.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.6.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

15. CALCULATIONS

15.1. The relative response factor is calculated as follows:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: RRF = relative response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
C_{is} = concentration of internal standard in µg/L.
A_{is} = area of the characteristic ion for internal standard.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RRF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RRFs for the target analyte.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RRF_{ave} - RRF_{daily}|}{RRF_{ave}} \times 100$$

where: %D = percent difference.
RRF_{daily} = daily RRF for the target analyte.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.4. The percent drift of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent drift.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.
Note: Concentrations must be in equivalent units.

15.5. The relative retention time of each target analyte is calculated as follows:

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.
RT_x = retention time of target analyte.
RT_{is} = retention time of internal standard.

Note: Retention times are in minutes to three decimal places.

15.6. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.7. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.8. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.9. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RRF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of internal standard in µg/L.
A_{is} = area of the characteristic ion for internal standard.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.10. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_p \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
For lower limit of quantitation, V_p = 20.
V_A = volume of aqueous sample purge-and-trap extracted in mL.
D = dilution factor, if the aqueous sample was serially diluted prior to purge-and-trap extraction. If no dilution was made, D = 1.

15.11. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
W_S = mass of solid sample purge-and-trap extracted in g.

15.12. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
W_S = mass of solid sample purge-and-trap extracted in g.
C_{ss} = solids content in %.

15.13. The target analyte concentration for a methanol extracted solid (or oil) sample without moisture correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_1}{V_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
V_S = volume of methanol extract purge-and-trap extracted in mL.

P_1 = preparation factor without moisture correction for methanol extracted solid (or oil) sample in mL/g.

15.14. The target analyte concentration for a methanol extracted solid sample without methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_2}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_2 = preparation factor without methanol/water dilution factor correction for methanol extracted solid sample in mL/g.

15.15. The target analyte concentration for a methanol extracted solid sample with methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_3}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_3 = preparation factor with methanol/water dilution factor correction for methanol extracted solid sample in mL/g.

15.16. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_p \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in mg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_p = purge volume in mL.
Unless specified otherwise, V_p = 5.
V_{MP} = volume of mobility-procedure extract purge-and-trap extracted in mL.
D = dilution factor, if the mobility-procedure extract was serially diluted prior to purge-and-trap extraction.
If no dilution was made, D = 1.

15.17. Refer to the preparatory method(s) for additional calculations.

15.18. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

15.18.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.19. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ▶POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this

situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

18.1.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

18.2. The acceptance criteria for LCS compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS compound are based upon the historical average recovery ± 3S that is updated at least annually. All LCS compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. For EPA Region 9 requirement, refer to Section 12.5.3.1.2. and Section 12.5.3.1.3. for acceptance criteria.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD ***(when applicable)*** is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.3. ***If the LCS/LCSD is used in place of the MS/MSD due to insufficient sample amount, or if LCS/LCSD is required per client or project specific DQO, both the LCS and LCSD data must be reported.***

18.3. The acceptance criteria for surrogate compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. and Section 12.6.2.1.3. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.4. Unacceptable surrogate recoveries do not necessarily invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same sample should be re-processed and re-analyzed.

18.3.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

18.3.4.3.1. If upon re-processing and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.4.1. For EPA Region 9 requirement, refer to Section 12.6.4.1.2. and Section 12.6.4.1.3. for acceptance criteria.

18.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for

the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique.

18.6. Additional information regarding internal quality control checks is provided in ***the current revision of*** SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. ▶CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ▶CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples.

20.1.2. LCS: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the ***group leader*** confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, ***refer to the current revision of SOP-T020 for procedures on data reporting and corrective action***.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8260B, USEPA, Revision 2, December 1996.

22.2. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.6. *Volatile Organic Compounds (VOCs)*, SW-846 Method 8260, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ►Appendix A: List of Primary and Secondary Ions of Target Analytes, Surrogates, and Internal Standards.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

23.3. Appendix C: Control Limits for Department of Defense Project.

23.4. ***►Appendix D: Requirements for Low Level 1,2,3,-Trichloropropane (TCP) and 1,4-Dioxane Determined by EPA 8260B Using Selected Ion Monitoring (SIM) Mode.***

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8260B Revision 2 are noted.

Calscience SOP M311 Section	Reference Document EPA Method 8260B Section	Summary of Modification
12.2.	7.3	The requirement of providing the data user a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded the specified limit is modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
0.1	Section 3: Update terminology for RL and add reference to the determinations of DL and RL. Section 4: Revise the scope to include additional analytes, and update EPA method numbers. Section 5: Update EPA method numbers. Section 6: Add LOD and LOQ definitions. Section 7: Update interferences.	K. Chang	08/17/12

Revision	Description	Author(s)	Effective Date
0.1	Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation. Section 11: Revise the requirements on preservation, headspace, and container. Section 12: Revise quality control criteria. Section 13: Revise subtitles. Section 14: Revise tuning and data reporting procedures. Section 18: Update section references, and add EPA Region 9 requirements. Section 24: Revise modifications. Section 25: Add revision history. Appendix A: Update the ion list for additional analytes. Appendix B: Update DoD quality control requirements and criteria.	K. Chang	08/17/12
0.2	Correct minor typos/grammar throughout. Section 4: Delete unused prep methods. Section 6: Update "batch" definition. Section 9: Revise equipment. Section:10: Update calibration tables Section 11: Revise sample preservation and storage. Section 12: Revise quality control criteria. Section 14: Revise LCSD requirement. Section 18: Revise LCSD requirement. Section 25: Update Revision History. Appendix A: Update the ion table.	I. Kwak / L. Hunt	08/12/13
0.3	Entire document: Update company name.	L. Hunt	03/09/15
0.4	Section 6: Update definitions. Sections 8 and 17: Add SDS. Section 10: Update calibration standards. Sections 12 and 14: Update LCSD requirement. Section 14: Add prescreening procedure. Appendix A: Update ions. Appendix D: Delete BP criteria appendix and replace with requirements for low level 1,2,3,-TCP and 1,4-dioxane by 8260B SIM.	Y. Patel / L. Hunt	03/18/15

►Appendix A

LIST OF PRIMARY AND SECONDARY IONS OF TARGET ANALYTES, SURROGATES, AND INTERNAL STANDARDS

Eurofins Calscience, Inc.

►Appendix A

Primary and Secondary Ions

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
acetone	58	43
acetonitrile	41	40
acrolein	56	55
acrylonitrile	53	52 , 51
allyl chloride	76	41 , 40 , 78
tert-amyl methyl ether (TAME)	73	87 , 55
benzene	78	51
bromobenzene	156	77 , 158
bromochloromethane	***130***	***128***
bromodichloromethane	83	85 , 127
1,4-bromofluorobenzene (surrogate)	95	174
bromoform	173	175 , 254
bromomethane	94	96
1,3-butadiene	54	53 , 39
2-butanone	***43***	***72***
tert-butyl alcohol (TBA)	59	57 , 41
tert-butyl alcohol-d_9 (internal standard)	65	66
n-butylbenzene	91	92 , 134
sec-butylbenzene	105	134
tert-butylbenzene	134	119 , 91
carbon disulfide	76	78
carbon tetrachloride	117	119
chlorobenzene	112	77 , 114
chlorobenzene-d_5 (internal standard)	117	82
chloroethane	64	66
2-chloroethyl vinyl ether	63	65 , 106
chloroform	83	85
chloromethane	50	52
chloroprene	53	88 , 90 , 51
1-chloropropane	42	41 , 39
2-chloropropane	43	41 , 39 , 63
2-chlorotoluene	91	126
4-chlorotoluene	91	126
cyclohexane	84	56 , 41 , 55
cyclohexanone	55	69 , 98 , 42
dibromochloromethane	129	127

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
1,2-dibromo-3-chloropropane	75	155
1,2-dibromoethane	107	109 , 188
dibromofluoromethane (surrogate)	113	111
dibromomethane	93	95 , 174
1,2-dichlorobenzene	146	111 , 148
1,3-dichlorobenzene	146	111 , 148
1,4-dichlorobenzene	146	111 , 148
1,4-dichlorobenzene-d_4 (internal standard)	152	150
trans-1,4-dichloro-2-butene	53	88 , 75
dichlorodifluoromethane	85	87
1,1-dichloroethane	63	65 , 83
1,2-dichloroethane	62	98 , 64 , 49
1,2-dichloroethane-d_4 (surrogate)	65	102 , 67
1,1-dichloroethene	***61***	***96*** , ***95***
cis-1,2-dichloroethene	96	61 , 98
trans-1,2-dichloroethene	96	61 , 98
1,2-dichloropropane	63	112
1,3-dichloropropane	76	78
2,2-dichloropropane	77	97
1,1-dichloropropene	75	110 , 77
cis-1,3-dichloropropene	75	77 , 39
trans-1,3-dichloropropene	75	77 , 39
diethyl ether	***59***	***74*** , ***45***
1,4-difluorobenzene (internal standard)	114	88
diisopropyl ether (DIPE)	45	87
1,4-dioxane	88	58 , 43 , 57
ethanol	45	46 , 43
ethylbenzene	91	106
ethyl tert-butyl ether (ETBE)	59	87
ethyl methacrylate	69	41 , 99
hexachloro-1,3-butadiene	225	223 , 227
hexane	57	56 , 43 , 41
2-hexanone	43	58
iodomethane	142	127 141
isobutyl alcohol (iso-butanol)	43	41 , 42 , 74
isopropanol (2-propanol)	45	59

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
isopropylbenzene	105	120
p-isopropyltoluene	119	91 , 134
methacrylonitrile	41	67
methyl acetate	43	74 , 59
methyl tert-butyl ether (MTBE)	73	57
methyl methacrylate	69	41 , 100 , 39
2-methyl-2-butanone (TAA)	59	55 , 73
methylcyclohexane	83	55 , 98 , 41
methylene chloride	84	86
4-methyl-2-pentanone (MIBK)	***58***	***85***
naphthalene	128	127
pentafluorobenzene (internal standard)	168	137
propanedinitrile	66	38 , 39 , 65
propionitrile	54	52 , 55 , 40
n-propylbenzene	91	120
styrene	104	78
1,1,1,2-tetrachloroethane	131	133 , 119
1,1,2,2-tetrachloroethane	83	131 , 85
tetrachloroethene	***166***	***164*** , 131
tetrahydrofuran	42	41 , 71 , 72
thiophene	84	58 , 45
toluene	***91***	***92***
toluene-d_8 (surrogate)	98	100
1,2,3-trichlorobenzene	180	182 , 145
1,2,4-trichlorobenzene	180	182 , 145
1,1,1-trichloroethane	97	99 , 61
1,1,2-trichloroethane	83	97 , 85
trichloroethene	95	97 , 130 , 132
trichlorofluoromethane	101	103
1,2,3-trichloropropane	***75***	***112*** , ***77***
1,1,2-trichloro-1,2,2-trifluoroethane	101	151 , 153
2,2,4-trimethyl pentane	57	56 , 41
1,2,4-trimethylbenzene	105	120
1,3,5-trimethylbenzene	105	120
vinyl acetate	***86***	***43***
vinyl chloride	62	64

Appendix A

Primary and Secondary Ions (Cont.)

o-xylene	*91*	*106*
p/m-xylenes	*91*	*106*

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., ion abundance, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average RRF for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.3.2. If the %RSD criterion for an analyte is not met, employ one of the following calibration options.

5.3.2.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.995.

5.3.2.1.1. Calibration may not be forced through the origin.

5.3.2.2. The second calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.990.

5.3.2.2.1. This option requires at least six calibration levels.

5.4. Initial Calibration Verification (ICV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to begin. Document the unacceptable result, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement of standard solutions or instrument maintenance, and recalibrate.

5.5. Continuing Calibration Verification (CCV)

5.5.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.5.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective actions and recalibrate.

5.5.3. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.6. Retention Time Window

5.6.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

5.6.1.1. Absolute retention time window for each analyte/surrogate is determined from the elution time of the analyte/surrogate in the midpoint calibration standard.

5.6.1.2. Document the serial number of the analytical column associated with the retention time window.

5.6.1.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

5.7. Event Based Quality Control (MBs and LCSs)

5.7.1. Method Blanks (MBs)

5.7.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.7.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.7.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.7.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.7.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.7.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.7.2. Laboratory Control Samples (LCSs)

5.7.2.1. The lower and upper acceptance limits for %REC of each LCS compound in aqueous and solid matrices are listed in Appendix C.

5.7.2.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.7.2.3. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.8. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

5.8.1. Surrogates

5.8.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix C.

5.8.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.8.2. Internal Standards

5.8.2.1. If the EICP area of any internal standard in each standard, sample, and blank is not within −50% to +100% from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

5.8.2.2. If the retention time of any internal standard in each standard, sample, and blank is not within ± 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

5.8.2.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

5.8.2.4. If corrective action fails in a field sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

5.8.3. Matrix Spikes (MS/MSDs)

5.8.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix C. The RPD is ≤ 30%.

5.8.3.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.8.3.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 20 per batch, excluding QC check samples and MBs)
5) Matrix Spike (MS)

6) Matrix Spike Duplicate (MSD)

6.1.1. Item 6: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 7: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix C

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	80	130	75	135
1,1,1-Trichloroethane	65	130	55	145
1,1,2,2-Tetrachloroethane	65	130	55	140
1,1,2-Trichloroethane	75	125	65	135
1,1-Dichloroethane	70	135	60	145
1,1-Dichloroethene	70	130	55	140
1,1-Dichloropropene	75	130	65	140
1,2,3-Trichlorobenzene	55	140	45	155
1,2,3-Trichloropropane	75	125	65	130
1,2,4-Trichlorobenzene	65	135	55	145
1,2,4-Trimethylbenzene	75	130	65	140
1,2-Dibromo-3-chloropropane	50	130	35	145
1,2-Dibromoethane	80	120	75	125
1,2-Dichlorobenzene	70	120	60	130
1,2-Dichloroethane	70	130	60	140
1,2-Dichloropropane	75	125	65	135
1,3,5-Trimethylbenzene	75	130	65	140
1,3-Dichlorobenzene	75	125	65	130
1,3-Dichloropropane	75	125	65	135
1,4-Dichlorobenzene	75	125	65	130
2,2-Dichloropropane	70	135	60	150
2-Butanone	30	150	10	170
2-Chlorotoluene	75	125	65	135
2-Hexanone	55	130	45	140
4-Chlorotoluene	75	130	65	135
4-Methyl-2-pentanone (MIBK)	60	135	45	145
Acetone	40	140	20	160
Benzene	80	120	75	130
Bromobenzene	75	125	70	130
Bromochloromethane	65	130	55	140
Bromodichloromethane	75	120	70	130
Bromoform	70	130	60	140
Bromomethane	30	145	10	165
Carbon disulfide	35	160	15	185
Carbon tetrachloride	65	140	55	150
Chlorobenzene	80	120	75	130
Chlorodibromomethane	60	135	45	145
Chloroethane	60	135	50	145
Chloroform	65	135	50	150
Chloromethane	40	125	25	140
cis-1,2-Dichloroethene	70	125	60	135
cis-1,3-Dichloropropene	70	130	60	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	125	65	135
Dichlorodifluoromethane	30	155	10	175
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	50	140	35	160
Isopropylbenzene	75	125	65	135
m,p-Xylene	75	130	65	135
Methyl tert-butyl ether (MTBE)	65	125	55	135
Methylene chloride	55	140	40	155
Naphthalene	55	140	40	150
n-Butylbenzene	70	135	55	150
n-Propylbenzene	70	130	65	140
o-Xylene	80	120	75	130
p-Isopropyltoluene	75	130	65	140
sec-Butylbenzene	70	125	65	135
Styrene	65	135	55	145
tert-Butylbenzene	70	130	60	140
Tetrachloroethene	45	150	25	165
Toluene	75	120	70	130
trans-1,2-Dichloroethene	60	140	45	150
trans-1,3-Dichloropropene	55	140	40	155
Trichloroethene	70	125	60	135
Trichlorofluoromethane	60	145	45	160
Vinyl chloride	50	145	35	165

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	75	125	65	135
1,1,1-Trichloroethane	70	135	55	145
1,1,2,2-Tetrachloroethane	55	130	40	145
1,1,2-Trichloroethane	60	125	50	140
1,1-Dichloroethane	75	125	65	135
1,1-Dichloroethene	65	135	55	150
1,1-Dichloropropene	70	135	60	145
1,2,3-Trichlorobenzene	60	135	50	145
1,2,3-Trichloropropane	65	130	50	140
1,2,4-Trichlorobenzene	65	130	55	140
1,2,4-Trimethylbenzene	65	135	55	145
1,2-Dibromo-3-chloropropane	40	135	25	150
1,2-Dibromoethane	70	125	60	135
1,2-Dichlorobenzene	75	120	65	125
1,2-Dichloroethane	70	135	60	145
1,2-Dichloropropane	70	120	65	125
1,3,5-Trimethylbenzene	65	135	55	145
1,3-Dichlorobenzene	70	125	65	135
1,3-Dichloropropane	75	125	70	130
1,4-Dichlorobenzene	70	125	65	135
2,2-Dichloropropane	65	135	55	145
2-Butanone	30	160	10	180
2-Chlorotoluene	70	130	60	140
2-Hexanone	45	145	30	160
4-Chlorotoluene	75	125	65	135
4-Methyl-2-pentanone (MIBK)	45	145	30	165
Acetone	20	160	10	180
Benzene	75	125	65	135
Bromobenzene	65	120	55	130
Bromochloromethane	70	125	60	135
Bromodichloromethane	70	130	60	135
Bromoform	55	135	45	150
Bromomethane	30	160	10	180
Carbon disulfide	45	160	30	180
Carbon tetrachloride	65	135	55	145
Chlorobenzene	75	125	65	130
Chlorodibromomethane	65	130	55	140
Chloroethane	40	155	20	175
Chloroform	70	125	65	135
Chloromethane	50	130	40	140
cis-1,2-Dichloroethene	65	125	55	135
cis-1,3-Dichloropropene	70	125	65	135

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	130	65	135
Dichlorodifluoromethane	35	135	15	155
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	55	140	40	155
Isopropylbenzene	75	130	70	140
m,p-Xylene	80	125	70	135
Methylene chloride	55	140	40	155
Naphthalene	40	125	25	140
n-Butylbenzene	65	140	50	150
n-Propylbenzene	65	135	50	145
o-Xylene	75	125	70	135
p-Isopropyltoluene	75	135	65	140
sec-Butylbenzene	65	130	50	145
Styrene	75	125	65	135
tert-Butylbenzene	65	130	55	145
Tetrachloroethene	65	140	55	150
Toluene	70	125	60	135
trans-1,2-Dichloroethene	65	135	55	145
trans-1,3-Dichloropropene	65	125	55	140
Trichloroethene	75	125	70	130
Trichlorofluoromethane	25	185	10	215
Vinyl chloride	60	125	45	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
1,2-Dichloroethane-d_4	70	120
4-Bromofluorobenzene	75	120
Dibromofluoromethane	85	115
Toluene-d_8	85	120

DoD Control Limits of Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
4-Bromofluorobenzene	85	120
Toluene-d_8	85	115

Appendix D

REQUIREMENTS FOR LOW LEVEL 1,2,3-TRICHLOROPROPANE (TCP) AND 1,4-DIOXANE DETERMINED BY EPA 8260B USING SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. ***EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Determination of Low Level 1,2,3-TCP and 1,4-Dioxane in Selected Ion Monitoring (SIM) Mode.***

2. APPLICABLE MATRICES

2.1. ***This method is applicable to soil/solid and aqueous matrices.***

3. DETECTION / QUANTITATION LIMITS

3.1. ***The reporting limits (RLs) for this method are as follows:***

	Water	Soil
1,2,3-TCP	0.005 µg/L	0.02 µg/kg
1,4-Dioxane	1.000 µg/L	5.00 µg/kg

3.2. ***The RLs will be proportionally higher for samples which require dilution or reduced sample size.***

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. METHOD SUMMARY

4.1. ***This analysis is performed using purge and trap and GC/MS.***

4.2. ***1,2,3-TCP and 1,4-dioxane are identified by matching the retention time and fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-trichloropropane-d_5 (1,2,3-TCP-d_5) and 1,4-dioxane-d_8 are used as the internal standards, which are added at the same concentration to the samples and standards.***

5. REAGENTS AND STANDARDS

5.1. ***The working calibration standard solution containing 50 ppm of 1,4-dioxane and 0.05 ppm of 1,2,3-TCP in methanol is used to prepare calibration standards.***

5.2. ***Inject the appropriate volume of the 0.05–50 ppm working calibration standard into 25 mL of reagent water for a water matrix analysis and into 5 mL water for a soil matrix analysis for initial calibration.***

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
1,4-Dioxane	500	500	50.0	5.00
1,2,3-Trichloropropane	0.5		0.05	

5.3. ***Use the following calibration levels as guidance to prepare the calibration standards for water matrix calibration using 25 mL purge.***

Analyte	Standard Compound Concentration (ug/L)						
123-TCP			0.005	0.01	0.02	0.05	0.10
1,4 - Dioxane	1.0	2.0	5.0	10.0	20.0	50.0	100.0
123-TCP-d5(IS)	0.04	0.04	0.04	0.04	0.04	0.04	0.04
1,4-Diox-d8(IS)	20	20	20	20	20	20	20
1,4-Dichlorobutane(S)	8	8	8	8	8	8	8

5.4. ***Use the following calibration levels as guidance to prepare the calibration standards for soil matrix calibration using 5.0 mL purge.***

Analyte	Standard Compound Concentration (ug/Kg)						
123-TCP		0.01	0.020	0.05	0.10	0.20	0.40
1,4 - Dioxane	5.0	10.0	20.0	50.0	100.0	200.0	400.0
123-TCP-d5(IS)	0.04	0.04	0.04	0.04	0.04	0.04	0.04
1,4-Diox-d8(IS)	20	20	20	20	20	20	20
1,4-Dichlorobutane(S)	8	8	8	8	8	8	8

5.4.1. ***The mid-range standards are also used as the continuing calibration verification solutions.***

5.5. ***The internal standards 1,2,3-trichloropropane-d_5 and 1,4-dioxane-d_8 and surrogate standard 1,4-dichlorobutane at concentrations of 10, 5000, and 2000 µg/mL concentration, respectively, is used to make working IS+SS mix in methanol for spiking all samples and QC samples including MB before analysis. The internal standard concentration in the working standard is 0.040 ppb for 123-TCP-d_5 and 20 ppb for 1,4-dioxane-d_8 and 8 ppb concentration for surrogate 1,4-dichlorobutane.***

5.5.1. ***Use the first run instrument blank with BFB from working 8260 internal/surrogate standard solution as the tuning standard solution.***

5.5.2. ***This procedure is possible due to split ratio configured for GC that allows the purge or injection of 5–50 ng of BFB as specified by the test methods.***

5.5.3. ***The initial calibration verification (ICV) solution contains the appropriate concentration of each target analyte, 8 ppb of the***

surrogate, 20 ppb of internal standard 1,4-dioxane-d_8, and 0.040 ppb of 1,2,3-TCP-d_5 in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration.

5.5.4. ***Use the following calibration level as guidance to prepare the ICV solution for water matrix.***

Analyte	ICV Concentration in ppb (µg/L)
1,2,3-TCP	0.02
1,4-Dioxane	20.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.5. ***Use the following calibration level as guidance to prepare the ICV solution for soil matrix.***

Analyte	ICV Concentration in ppb (µg/kg)
1,2,3-TCP	0.10
1,4-Dioxane	100.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.6. ***The continuing calibration verification (CCV) solution contains the appropriate concentration of each target analyte, 8 ppb of the surrogate, 20 ppb of internal standard 1,4-dioxane-d_8 and 0.040 ppb of 1,2,3-TCP-d_5 in reagent water. The CCV solution must be of the same source as that used for the initial multi-point calibration.***

5.5.7. ***Add the appropriate volumes of the working standards and the appropriate volume of the surrogate and internal standard working standard to 25 mL of reagent water, and purge and trap for continuing calibration verification.***

5.5.8. ***Use the following calibration level as guidance to prepare the CCV solutions for water matrix.***

Analyte	CCV Concentration in ppb (µg/L)
1,2,3-TCP	0.02
1,4-Dioxane	20.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.9. ***Use the following calibration level as guidance to prepare the CCV solution for soil matrix.***

Analyte	CCV Concentration in ppb (µg/kg)
1,2,3-TCP	0.10
1,4-Dioxane	100.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.9.1. ***One CCV solution is used daily for every tune batch of 12 hrs.***

5.5.10. ***For Water: The surrogate and internal standard working standard solution containing 1 ppm of 123-TCP-d_5 (IS), 500 ppm of 1,4-dioxane-d_8 (IS) and 200 ppm 1,4-dichlorobutane (S) are prepared in methanol for water matrix.***

5.5.11. ***For Soil: The surrogate and internal standard working standard solution containing 0.2 ppm of 123-TCP-d_5 (IS), 100 ppm of 1,4-dioxane-d_8 (IS) and 40 ppm 1,4-dichlorobutane (S) are prepared in methanol for soil matrix.***

5.6. ***If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the either water or soil surrogate and internal standard working standard into each aliquot for water or soil matrix sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction.***

6. QUALITY CONTROL

6.1. ***Hardware Tuning***

6.1.1. ***Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the BFB tune acceptance criteria as described earlier for 8260B method, and criteria must be demonstrated every 12 hours.***

6.2. ***Initial Calibration (IC)***

6.2.1. ***The initial multi-point calibration must be established prior to the processing of samples.***

6.2.1.1. ***The calibration curve is established with five, six, or seven calibration standards.***

6.2.2. ***The IC is deemed valid if the %RSD for each analyte is ≤ 15%.***

6.2.3. ***If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.***

6.3. ***Initial Calibration Verification (ICV)***

6.3.1. ***The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.***

6.4. ***Continuing Calibration Verification (CCV)***

6.4.1. ***Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.***

6.4.2. ***The initial calibration is deemed valid if the following condition is met.***

6.4.2.1. ***The %D for each analyte is ≤ 20%.***

6.4.2.1.1. ***If the calibration option is average relative response, the %D is the percent difference.***

6.5. ***The internal standard response and retention time for the ICV and CCV must be evaluated during or immediately after data acquisition.***

6.5.1. ***If the EICP area of any internal standard in an ICV or CCV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.***

6.5.2. ***If the retention time of any internal standard in an ICV or CCV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.***

7. PROCEDURE

7.1. ***Instrument Setup***

7.1.1. ***Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.***

7.1.2. ***Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.***

Description	GC/MS Operating Condition
Mode	Splitless
Initial temp	200 ° C
Initial flow	0.8 mL/min
Purge flow	8.0 mL / min
Inlet pressure	13.53 psi
Split ratio	10:01
Split flow	8.0 mL/min
Total flow rate	11.6 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to130°C at 9.00°C/min 130°C to 230°C at 40.00°C/min
Run time	16.5 min
Transfer line temperature	260°C
SIM parameters	
Group ID	1
Resolution	Low
Group start time	2
Ions/Dwell	46/70
Ions/Dwell	58/70
Ions/Dwell	64/70
Ions/Dwell	88/70
Ions/Dwell	96/70
Group 2	2
Resolution	Low
Group start time	11
Ions/Dwell	55/30
Ions/Dwell	62/30

7.1.3. ***Use the following P & T operating conditions as guidance for running this method.***

Valve Oven Temp.:	150°C	Sample Preheat Time:	1.00 min.
Dry Purge Temp.:	20.0°C	Bake Time:	8.00 min.
Transfer Line Temp.:	150°C	Sample Temp.:	40.0°C
Dry Purge Flow:	150 mL/min.	Bake Temp.:	280°C
Sample Mount Temp.:	90.0 °C	Purge Time:	11.0 min.
GC Start:	Start of Desorb	Bake Flow:	40.0 mL/min.
Purge Ready Temp.:	40.0 °C	Purge Temp.:	0.0°C
Desorb Preheat Temp.:	245° C	Condenser Bake Temp.:	230°C
Standby Flow:	0.0 mL/min.	Purge Flow:	40 mL/min.
Desorb Drain:	On	Focus Temp.:	-150°C
Pre-Purge Time:	0.50 min.	Condenser Ready Temp.:	40.0°C
Desorb Time:	4.00 min.	Inject Time:	1.00 min.
Pre-Purge Flow:	40 mL/min.	Condenser Purge Temp.:	20.0°C
Desorb Temp.:	250°C	Inject Temp.:	180°C
Sample Heater:	Off	Dry Purge Time:	1.00 min.
Desorb Flow:	30 mL/min.	Standby Temp.:	100°C

7.1.3.1. ***123-TCP and 1,4-dioxane are identified by matching the retention time and fragment ions and ion abundances from the sample with those of the reference standard. Identification requires expert judgment, especially when sample components are not completely resolved, or if 123-TCP and/or 1,4-dioxane is present at very low concentration (near the detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve.***

Title : **1,4- Dioxane by GC/MS Isotope Dilution**

Document No. : SOP-M440
Revision No. : 1.2
Supersedes : 1.1

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PROPRIETARY INFORMATION STATEMENT

Revision 1.2 changes are noted in bold italicized typeface and preceded by a "►" marker

APPROVED FOR RELEASE BY:

_____	06/27/12
MANAGEMENT	**DATE**
_____	06-27-12
QA DEPARTMENT	**DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. 1,4-Dioxane by GC/MS Isotope Dilution.

2. APPLICABLE MATRICES

2.1. This method is applicable for water/aqueous matrices and soil/solids.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Soil/Solid (Low Level)	Water
0.2 mg/kg (0.025 mg/kg)	1.0 µg/L

3.2. The EQLs will be proportionally higher for sample extracts which require dilution.

4. SCOPE AND APPLICATION

4.1. This standard operating procedure is limited to the determination of 1,4-Dioxane (also known as p-Dioxane).

4.2. This method is restricted to use by or under the supervision of analysts and supervisors who are experienced in the use of GC/MS and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. 14-Dioxane is determined by the GC/MS isotope dilution method.

5.2. ►As an internal standard, 1,4-Dioxane-d_8 is added to ***1 L of an aqueous*** sample, or to 10 g of a solid sample. The aqueous sample is extracted at ***pH > 11*** using methylene chloride ***via continuous*** liquid-liquid technique. The final extract volume for the aqueous and solid samples is 2 mL.

5.3. 1,4-Dioxane is separated and identified by the GC and MS, respectively. Identification involves the comparison of the sample analysis retention times and background-corrected spectral masses to the 1,4-Dioxane standard.

5.4. Quantitation is performed using the extracted ion current profile (EICP) areas. Isotope dilution is used, as this is readily available. Otherwise, the internal standard method may be employed.

5.5. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Pressurized Fluid Extraction	3545	SOP-M204

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.13. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.28. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high-level samples should be analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the injector or column. To minimize this effect, guard columns should be used and cut or replaced frequently. Also, the column can be "baked" after such samples.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. As a matter of routine, sample extracts with a dark color or high viscosity are subject to column Florisil cleanup prior to injection. In this procedure, a glass column is packed with Florisil and topped with a water adsorbent. Using methylene chloride as the solvent, separation of the target analytes and interferents is effected. Using the solvent, the target analytes are eluted through the column while the Forisil retains the interferents.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Hewlett-Packard 6890 Series II Gas Chromatograph configured with a HP 7673A autoinjector and PC based data system or equivalent.

9.2. Instrument Software

9.2.1. Requires a PC based data system or equivalent.

9.2.2. Agilent Environmental MSD ChemStation Version E.02 or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. Mass Spectrometer: HP 5973 Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 500amu every one second or less, using 70 volts nominal electron energy in the EI mode or equivalent. The MSD must be capable of producing a mass spectrum for DFTPP that meets all of the criteria in Section 12.1.1 when 1 µL of the tuning standard (50 ng of DFTPP) is injected. The MS is directly coupled (capillary direct) to the column via a heated interface.

9.5. Column: HP-5 MS, 30m x 0.25mm ID, 0.50µ film thickness, and silicone coated fused-silica capillary column or equivalent.

9.6. Guard Column: 0.53mm, non-coated fused silica.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene chloride, CH_2Cl_2, pesticide grade or equivalent.

10.1.2. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v). Prepare the solution by dissolving granular $Na_2S_2O_3$ (reagent grade or equivalent) in reagent water.

10.1.3. Reagent water, interferant free.

10.1.4. Sand, washed, sea or standard Ottawa.

10.1.5. All reagents must be inspected, verified and documented prior to use.

10.2. Standards

10.2.1. Tuning standard solution contains 50ppm each of decafluorotriphenylphosphine (DFTPP), benzidine, pentachlorophenol, and 44'-DDT in methylene chloride.

10.2.1.1. A 1 µL injection of this solution is used for each tuning.

10.2.2. Pre-certified neat solutions of 1,4-Dioxane sealed in glass ampules, and 2000 ppm of surrogate, are used to prepare 0.5, 20, 80, 120, and 160 ppm calibration standards. 1,4-Dioxane-d8 and Nitrobenzene-d8 at 40 ppm are used as the internal standards. An 80 ppm 1,4-Dioxane solution is also used as the mid-range standard for calibration verification (CV).

10.2.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
1,4-Dioxane	0.5	20	80	120	160
1,4-Dioxane-d_8 (IS)	40	40	40	40	40
Naphthalene-d_8 (IS)	40	40	40	40	40
Nitrobenzene-d_5 (S)	0.5	20	80	120	160

10.2.2.2. The expiration date of each calibration standard is set equivalent to the expiration date of the stock standard(s) that will expire first.

10.2.3. Initial calibration verification (ICV) solution contains 80 ppm of 1,4-Dioxane, the surrogate compound, and 40 ppm of the internal standards. The ICV solution must be of a source other than that used for the initial five-point calibration.

10.2.3.1. The ICV solution is prepared as follows:

Analyte	Standard Compound Concentration (ppm)
1,4-Dioxane	80
1,4-Dioxane-d_8 (IS)	40
Naphthalene-d_8 (IS)	40
Nitrobenzene-d_5 (S)	80

10.2.4. Continuing calibration verification (CCV) solutions containing mid-range concentrations of target analyte, internal standards, compounds, and

surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

10.2.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
1,4-Dioxane	80
1,4-Dioxane-d_8 (IS)	40
Naphthalene-d_8 (IS)	40
Nitrobenzene-d_5 (S)	80

10.2.4.2. One CCV solution is used every tune batch of 12 hours or less.

10.2.5. Surrogate standard solution contains 400 ppm Nitrobenzene-d_5.

10.2.5.1. 500 µL of this solution is used for the surrogate spike.

10.2.6. The spike standard (MS/MSD) solution contains 1000 ppm 1,4-Dioxane.

10.2.6.1. 200 µL of this solution is spiked for MS/MSDs.

10.2.7. The LCS (LCS/LCSD) standard solution contains 1000 ppm 1,4, -Dioxane.

10.2.7.1. 200 µL of this solution is spiked for LCS/LCSDs.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1L pre-cleaned amber glass containers with Teflon-lined closures. Samples should be maintained in a chilled state (> 0°C to ≤ 6°C) post-collection, until received at the laboratory. Soil samples should be collected in 4-oz, pre-cleaned, clear, and wide-mouth jars with Teflon-lined closures. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.2. Upon receipt, the samples are stored in a cooler (> 0°C to ≤ 6°C). Aqueous samples must be extracted within seven (7) days of collection.

11.3. All extracted samples are then stored under refrigerated (4°C) conditions, and must be analyzed within a 40-day period following extraction.

12. QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standard(s), the GC/MS DFTPP tuning standard must be analyzed and meet the following acceptance criteria:

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 - 60% of mass 198
197	< 1% of mass 198

Mass	Ion Abundance Criteria
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 - 23% of mass 442

12.1.2. These criteria must be demonstrated every 12 hours.

12.1.3. If a tune does not meet the acceptance criteria, correct the problem and re-tune the system.

12.1.4. Whenever invasive maintenance of the GC/MS hardware is performed, the system must be re-tuned.

12.2. Initial Calibration

12.2.1. The initial calibration must be established prior to the processing of sample extracts.

12.2.2. The %RSD for 1,4-Dioxane should be less than or equal to 15%. Where the %RSD is ≤15%, then the relative response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation. If this criterion is not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.3. The relative retention time (RRT) should agree to within 0.06 RRT units. This is not a requirement but non-compliance should be considered indicative of a problematic calibration for the affected target analytes.

12.3. Initial Calibration Verification (ICV)

12.3.1. The ICV is deemed valid if the %D for 1,4-Dioxane and Nitrobenzene-d_5 is ≤ 20%. If the criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation standard solutions, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following establishment of a valid initial calibration, a CCV standard must be analyzed every 12 hours thereafter during analysis. If the 1,4-Dioxane and Nitrobenzene-d_5 criteria are met for this CCV, the initial calibration is assumed to be valid and sample analysis may resume.

12.4.2. The CCV is deemed valid if the %D for 1,4-Dioxane and Nitrobenzene-$_{d5}$ is ≤ 20%. If the criteria are not met, the CCV is deemed unacceptable for sample analysis to resume. Reanalyze the CCV.

12.4.3. The internal standard response and retention time in the CCV must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the mid-point standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the mid-point standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.4. If these criteria are not met, than all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

12.4.5. It is a useful diagnostic tool to monitor internal standard retention times and area counts in all samples, spikes, blanks, and standards to check drifting method performance and monitor system trends.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected. If the problem was not related to the extraction process, then the LCS/LCSD and all associated sample extracts must be re-analyzed. If the failure was associated with the extraction process, then all associated samples must be re-extracted and re-analyzed.

12.5.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.5.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment, administered by the Group Leader and/or the Technical Director, should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

12.6. Sample Based Quality Control (Surrogates and MS/MSDs)

12.6.1. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

12.6.1.1. If the surrogate compound recovery is acceptable, report the surrogate and sample data without qualification.

12.6.1.2. If the surrogate recovery is not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.1.3. By itself, an unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if the surrogate recovery is not acceptable.

12.6.1.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

12.6.1.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recovery, the same extract should be re-analyzed.

12.6.1.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recovery, the affected sample(s) must be re-extracted and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recovery and the sample data reported with qualification.

12.6.1.3.3.1. If, upon re-extraction and re-analysis, the surrogate remains unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recovery and the sample data reported with qualification.

12.6.1.3.3.2. If the MB surrogate is unacceptable, all associated sample data must invalidated and all associated samples re-extracted and re-analyzed.

12.6.1.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery, which must be reported to the client.

12.6.2. The acceptance criteria for MS/MSDs are as follows:

12.6.2.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.2.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.3. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Prior to the analysis of sample or QC extracts, the GC/MS system must be hardware tuned and an initial five-point calibration established. The acceptance criteria for the parameters are listed below in Section 12, Quality Control.

13.1.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired no more 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

13.2. Calibration Verification: Upon obtaining an acceptable five-point calibration curve and prior to processing samples, an initial calibration verification (ICV) analysis must be conducted to verify the initial calibration standards.

13.2.1. The ICV shall be at mid-concentration containing 1,4-Dioxane and shall be of a source other than that of the initial calibration. The acceptance criteria for the ICV are listed below in the Section 12, Quality Control.

13.3. The initial five-point calibration and ICV should include 1,4-Dioxane for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Carrier gas flow rate	1 mL/min at 7.15 psi
Initial temperature	40°C, hold 1.50 min
Temperature program	40°C to 280°C at 22.00°C/min 280°C to 310°C at 5.00°C/min
Final temperature	310°C, hold 6.00 min
Transfer line temperature	285°C
Scan range	35~550 amu

14.1.2. Auto injector is set to inject 1 µL of sample or QC extract.

14.2. Following establishment of a valid initial calibration, calibration verification (CV) standard must be analyzed every 12 hours thereafter during analysis. The acceptance criteria for the CV are listed below in Section 12, Quality Control.

14.3. Following extraction by one of the methods specified in Section 5.5, the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC/MS sample tray.

14.4. The sample vials may be loaded in the following order or in any other acceptable order.

1) Tuning Standard
2) Calibration Verification (CV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: See Section 10.2.1. An acceptable tune demonstrates acceptable hardware performance. A tune meeting the acceptance criteria is required at least every 12 hours.

14.4.2. Item 2: See Section 10.2.2. A CV is used to verify the acceptance of the initial five-point calibration on a continuing basis. Similar to the initial five-point calibration, only the 1,4-Dioxane is monitored for acceptance. An acceptable CV is required at least every 12 hours.

14.4.3. Item 3: The LCS is a known matrix that has been spiked with a known concentration of the 1,4-Dioxane. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the

processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of 1,4-Dioxane spiked into clean water. For solid samples, the LCS consists of 1,4-Dioxane spiked into washed sea sand.

14.4.3.2. A LCS is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15, Calculations.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed that is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, internal standards, etc.).

14.4.5.1. For aqueous samples, the MB consists of organic free water. For solid samples, the MB consists of washed sea sand.

14.4.5.2. A MB is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs or solvent blanks may be placed in the sequence.

14.4.5.2.1. When samples that are extracted together are analyzed on separate instruments and/or at different times, the MB associated with those samples must be analyzed on one of the instruments. A solvent blank should be analyzed on the other instruments to demonstrate that the instrument is not introducing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrumentation is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.7. Item 7: The MS is the actual matrix spiked with known concentrations of the 1,4-Dioxane. The sample that is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of a MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15, Calculations.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof extracted concurrently. This approach is considered "closed batch" as opposed to "open batch".

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15, Calculations.

14.5. Ensure that a sufficient amount of methylene chloride is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles. Specifically, ensure that the solvent rinse bottles are full and waste bottles are empty at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. The qualitative identification of analytes determined by this method is based on 1) elution of the sample component at the same relative retention time (RRT) as the standard component and 2) comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum. The reference mass spectrum should be obtained from the GC/MS within the same 12-hour period as the sample analysis. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.2. 1,4-Dioxane should be identified as present when:

14.8.2.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at a compound-specific retention time will be accepted as meeting this criterion.

14.8.2.2. The RRT of the sample target analyte is within ± 0.06 RRT units of the RRT of the standard target analyte.

14.8.2.3. The relative intensities of the characteristic ions agree with 30% of the relative intensities of these ions in the reference spectrum.

14.8.2.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.2.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one target analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When 1,4-Dioxane co-elutes, the identification criteria can be met, but each spectrum will contain extraneous ions contributed by the co-eluting compound.

14.8.3. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.8.3.1. If the %RSD of a target analyte's relative response factor is ≤ 15%, then the concentration in the extract may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating RF_{ave} is listed in Section 15, Calculations.

14.8.3.2. Alternatively, if the %RSD of a target analyte's relative response factor is > 15%, a regression line fitted to the initial calibration should be used for determination of the extract concentration.

14.8.3.2.1. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided in the below subsections are for the purpose of understanding.

14.8.3.2.2. The concentration of the analyte in an aqueous sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the volume of sample extracted. The formula for calculating the concentration is listed below in Section 15, Calculations.

14.8.3.2.3. The concentration of the analyte in the solid or oil phase of the sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the weight of the subsample. The formula for calculating the concentration is listed below in Section 15, Calculations.

14.8.3.3. Upon request, a library search may be made for the purpose of tentative identification of compounds not associated with the calibration standards. Refer to SOP-T025.

15. CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_{is} = concentration of the specific internal standard
C_x = concentration of the target analyte being measured in ng/µL.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the average RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each CCC is calculated as follows:

$$\%D = \frac{(C_I - C_c)}{C_I} \times 100$$

where: %D = percent difference (or percent drift) of CCC.
C_I = CCC standard concentration.
C_c = measured concentration.

Note: Concentrations must be in equivalent units.

15.4. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.7. Compound concentration in the extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the specific internal standard in ng/µL.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of 5 initial RFs for a compound.

15.8. Sample concentration for aqueous samples is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex}}{V_o}$$

where: C_A = concentration of the target analyte in the aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = extract volume in mL.
V_o = volume of aqueous sample extracted in L.

15.9. Sample concentration for solid (or oil) samples is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex}}{W_s}$$

where: C_S = concentration of the target analyte in the solid sample in mg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = extract volume in mL.
W_s = weight of solid sample extracted in kg.

15.10. All concentrations shall be reported in µg/L (ppb) for water samples and mg/kg (ppm) for oil, soil, and solid waste samples.

15.11. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for water samples and µg/kg (ppb) for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries are subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. US EPA, Test Methods for Evaluating Solid Waste, SW-846, Volume 1B, November 1986, SW-846, Third Edition; Volume 1B, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique" Revision 3, December 1996.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. None.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8270C are noted.

Calscience SOP M440 Section	Reference Document EPA Method 8270C Section	Summary of Modification
All	All	This is a modified method for 1,4-dioxane analysis by GC/MS isotope dilution.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.1	SOP updated. Section 6.0: Added LOD, LOQ. Section 9.2 and 9.3: Inserted instrument software version and maintenance information. Section 24: Modifications section added. Section 25: Add revision history.	Y. Patel	05/21/12
1.2	Section 5.2: Clarify extraction pH and technique.	Y. Patel	07/03/12

Title : **EPA METHOD 8270C, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

Document No. : SOP-M404
Revision No. : 4.9
Supersedes : 4.8

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PROPRIETARY INFORMATION STATEMENT

Revision 4.9 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/05/15
MANAGEMENT **DATE**

_____ 03-05-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature
	2/19/16		
	3/4/16		

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable to water/aqueous matrices, soil/solids, oil, sludges and hazardous waste.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Water	Oil
0.5 mg/kg (wet-weight)	10 µg/L	50 mg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Operation of the instrument in Selected Ion Monitoring (SIM) mode will allow a lower ***RL*** to be achieved for a specific analyte or suite of analytes. Optimization for a specific analyte or suite of analytes may be accompanied by other extractive or analytical modifications. Reference the appendices for available options and ***RLs***.

3.4. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedures on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. EPA Method 8270C is used to determine the concentration of a large number of semi-volatile organic compounds in various matrices. The method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. The following compounds may be determined by this method:

Base/Neutral Extractables

acenaphthene	2-chloronaphthalene	fluorene
acenaphthylene	4-chlorophenyl phenyl ether	hexachlorobenzene
anthracene	chrysene	hexachloro-1,3-butadiene
azobenzene	dibenz(a,h)anthracene	hexachlorocyclopentadiene
benzidine	1,2-dichlorobenzene	hexachloroethane
benzo(a)anthracene	1,3-dichlorobenzene	indeno(1,2,3-cd)pyrene
benzo(b)fluoranthene	1,4-dichlorobenzene	isophorone
benzo(k)fluoranthene	3,3'-dichlorobenzidine	naphthalene
benzo(a)pyrene	diethyl phthalate	nitrobenzene
benzo(g,h,i)perylene	dimethyl phthalate	n-nitrosodimethylamine
benzyl butyl phthalate	di-n-butyl phthalate	n-nitrosodiphenylamine
bis(2-chloroethyl)ether	di-n-octyl phthalate	n-nitrosodi-n-propylamine

bis(2-chloroethoxy)methane	2,4-dinitrotoluene	phenanthrene
bis(2-ethylhexyl)phthalate	2,6-dinitrotoluene	pyrene
bis(2-chloroisopropyl)ether	1,2-diphenylhydrazine	1,2,4-trichlorobenzene
4-bromophenyl phenyl ether	fluoranthene	
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)		

Acid Extractables

4-chloro-3-methylphenol	4,6-dinitro-2-methylphenol	pentachlorophenol
2-chlorophenol	2,4-dinitrophenol	phenol
2,4-dichlorophenol	2-nitrophenol	2,4,6-trichlorophenol
2,4-dimethylphenol	4-nitrophenol	

Hazardous Substances

aniline	dibenzofuran	2-nitroaniline
benzoic acid	2-methylnaphthalene	3-nitroaniline
benzyl alcohol	2-methylphenol	4-nitroaniline
4-chloroaniline	4-methylphenol	2,4,5-trichlorophenol

Others

pyridine	1-methylnaphthalene

Pesticides

aldrin	4,4'-DDE	endrin
α-BHC	4,4'-DDT	endrin aldehyde
β-BHC	4,4'-DDD	heptachlor
γ-BHC (lindane)	dieldrin	heptachlor epoxide
δ-BHC	endosulfan I	methoxychlor
α-chlordane	endosulfan II	toxaphene
γ-chlordane	endosulfan sulfate	

PCBs

aroclor-1016	aroclor-1242	aroclor-1260
aroclor-1221	aroclor-1248	aroclor-1262
aroclor-1232	aroclor-1254	

4.2. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8270C determination, either by regulatory reference or validation studies.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph / mass spectrometer (GC/MS) and skilled in the interpretation of mass spectra.

5. ►METHOD SUMMARY

5.1. EPA Method 8270C describes chromatographic procedures that will allow for the separation of the semi-volatile organic compounds in the extract and their qualitative and quantitative analysis by mass spectrometry. Detection is achieved using a mass selective detector either in Total Ion Scan (TIC) mode for full list reporting or Selected Ion Monitoring (SIM) mode for lower ***RL*** reporting for selected analytes.

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Soxhlet Extraction	3540C	SOP-M203
Pressurized Fluid Extraction	3545A	SOP-M204
Ultrasonic Extraction	***3550C***	SOP-M202
Waste Dilution	3580A	SOP-M205
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California)	T22.11.5.AII	SOP-M228

5.3. Solid samples are extracted via EPA Methods 3540C or ***3550C*** using methylene chloride, or via EPA Method 3545A using methylene chloride. Liquid samples are extracted via EPA Methods 3510C or 3520C at a neutral pH using methylene chloride. Oil samples are prepared in accordance with EPA Method 3580A using methylene chloride as the diluent. Solid samples for TCLP, SPLP, or STLC analysis are extracted using the appropriate extractant with the leachate then prepared by either separatory funnel or liquid-liquid extraction.

5.4. The extracts that are dirty and dark in color are subjected to Florisil cleanup.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.***

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.15. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.16. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.17. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.18. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.19. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.20. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.21. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.22. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.23. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.24. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.26. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the injector or analytical column. To minimize this effect, a guard columns should be used and cut frequently or replaced. Also, the analytical column can be "baked" after such samples.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. Plastics contain significant amounts of leachable phthalate esters and must not be used during any stage of analytic processing.

7.5. The following provides information regarding possible target analyte losses/interferences during analytic processing:

7.5.1. The base-neutral extraction may cause significantly reduced recoveries of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

7.5.2. Benzidine is subject to oxidative losses during extract concentration and poor chromatographic behavior.

7.5.3. Under the alkaline condition step of sample preparation, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

7.5.4. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

7.5.5. Depending upon chromatographic conditions and instrument setup, n-nitrosodimethylamine may be difficult to separate from the solvent.

7.5.6. N-nitrosodiphenylamine decomposes in the GC inlet and cannot be separated from diphenylamine.

7.5.7. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 4-chloroaniline, all nitroanilines, and benzyl alcohol are subject to erratic chromatographic

behavior. This effect is especially pronounced where the system contains high-boiling residue.

7.5.8. Pyridine may perform poorly (degrade) at normal injection port temperatures.

7.6. As a matter of routine prior to injection, all dirty or dark colored sample extracts for GC/MS determination are subjected to column Florisil cleanup. In this procedure, a glass column is packed with Florisil and topped with a water adsorbent. The methylene chloride solvent separates the target analytes from interferants by allowing the target analytes to elute through the column. Meanwhile, the Florisil retains the interferants.

8. ►SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

8.3. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzo(a) anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a) pyrene, dibenz(a,h) anthracene, and n-nitroso-dimethylamine. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph or equivalent configured with splitless injection port and Agilent 7673/7683 Series Autoinjector and PC based data system.

9.2. Mass Spectrometer: Agilent 5973/5973N Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 500 amu every one second or less, utilizing a 70-V nominal electron energy in the electron-impact ionization (EI) mode. The MS is directly coupled (capillary direct) to the column via a heated interface.

9.2.1. The MSD must be capable of producing a mass spectrum for DFTPP which meets all of the criteria in Section 12.1.1. when 1 µL of the tuning standard (50 ng of DFTPP) is injected.

9.3. Instrument Software

9.3.1. Requires a PC based data system or equivalent.

9.3.2. Agilent Environmental MSD ChemStation Version E.02 or equivalent.

9.4. Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 30-m × 0.25-mm ID, 0.5-µm (or 0.25-µm) film thickness, silicone coated fused-silica capillary column, HP-5 MS or equivalent.

9.6. Carrier Gas: High purity helium.

9.7. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with N.I.S.T. Traceable Certification.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene chloride, CH_2Cl_2, pesticide grade or equivalent.

10.1.2. Acetone, CH_3COCH_3, pesticide grade or equivalent.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v). Prepare the solution by dissolving granular $Na_2S_2O_3$ (reagent grade or equivalent) in reagent water.

10.1.4. Reagent water, interferant free.

10.1.5. Sand, washed, sea or standard Ottawa.

10.1.6. All reagents must be inspected and documented prior to use.

10.2. Standards

10.2.1. The tuning standard solution contains 50 ppm each of decafluorotriphenylphosphine (DFTPP), benzidine, pentachlorophenol, and 4,4'-DDT in methylene chloride.

10.2.1.1. Inject 1 µL of the tuning standard for hardware tuning.

10.2.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 200/2000 ppm of each target analyte, 5000 ppm of each base/neutral surrogate, 10000 ppm of each acid surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

10.2.3. Calibration standard solutions containing various concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride are used to prepare calibration standards.

10.2.3.1. The calibration standards are prepared as follows:

Analyte		Standard Compound Concentration (ppm)						
base/neutrals		5	10	20	50	80	120	160
acids	2.5*	5/10*	10/20*	20/40*	50/100*	80/160*	120/240*	160/320*
internal standards	40	40	40	40	40	40	40	40
surrogates		5	10	20	50	80	120	160

* 3/4-Methylphenol only.

10.2.3.2. The 10-ppm calibration standard is considered part of the initial multi-point calibration if an analyte yields poor response from the 5-ppm calibration standard.

10.2.3.3. The system performance check compounds (SPCCs) are n-nitrosodi-n-propylamine, hexachlorocyclopentadiene, 2,4-dintrophenol, and 4-nitrophenol.

10.2.3.4. The calibration check compounds (CCCs) are phenol, 1,4-dichlorobenzene, 2-nitrophenol, 2,4-dichlorophenol, hexachlorobutadiene, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, acenaphthene, n-nitrosodiphenylamine, pentachlorophenol, fluoranthene, di-n-octylphthalate, and benzo(a)pyrene.

10.2.3.5. The 50-, 80-, and 120-ppm standards are also used as the continuing calibration verification solutions.

10.2.4. The initial calibration verification (ICV) solution contains the midpoint concentration of each target analyte, internal standard, check compound, and surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.4.1. The ICV solution is prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

10.2.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5.2. One CCV solution is used daily.

10.2.6. The surrogate standard solution contains 400 ppm each of 2-fluorophenol, phenol-d_6, nitrobenzene-d_5, 2-fluorobiphenyl, 2,4,6-tribromophenol, and p-terphenyl-d_{14} in acetone or methylene chloride.

10.2.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.7. The internal standard solution contains 2000 ppm each of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

10.2.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

10.2.8. The spike standard solution contains 1000 ppm each of phenol, 2-chlorophenol, 1,4-dichlorobenzene, n-nitrosodi-n-propylamine, 1,2,4-trichlorobenzene, naphthalene, 4-chloro-3-methylphenol, dimethyl phthalate, acenaphthylene, acenaphthene, 4-nitrophenol, 2,4-dinitrotoluene, fluorene, pentachlorophenol, pyrene, and benzyl butyl phthalate in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.2. Add 200 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

10.2.9. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

10.2.10. All stock standards must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures. Soil samples should be collected in 4-oz. pre-cleaned

clear glass wide-mouth jars with Teflon-lined closures. Oil samples should be collected in 40-mL VOA vials with Teflon-lined closures.

11.1.1. Aqueous samples shall be preserved with 4 mL of 10% $Na_2S_2O_3$ solution per 1 L of sample to remove residual chlorine.

11.2. Samples should be maintained in a chilled state (≤ 6°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a cooler at temperature ≤ 6°C. Aqueous samples must be extracted within seven (7) days of collection. An extraction holding time of 14 days applies to all non-aqueous samples.

11.4. All extracted samples are then stored in freezer at (≤ -10°C) conditions and must be analyzed within a 40-day period post extraction.

12. QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the GC/MS DFTPP tuning standard must be analyzed and meet the following acceptance criteria:

Mass	Ion Abundance Criteria
51	30 – 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 – 60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 – 23% of mass 442

12.1.1.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

12.1.1.2. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

12.1.2. These criteria must be demonstrated every 12 hours.

12.1.3. If a tune does not meet the acceptance criteria, correct the problem and re-tune the system.

12.1.4. Whenever invasive maintenance of the GC/MS hardware is performed, the system must be re-tuned.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

12.2.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

12.2.3. Where the %RSD for each target analyte is ≤ 15%, the response factor is assumed to be invariant, and the average response factor may be used for quantitation.

12.2.4. In those instances where the %RSD for one or more target analytes exceeds 15%, the initial calibration remains acceptable if the following conditions are met:

12.2.4.1. The mean of the %RSD values for all analytes in the calibration is ≤ 15%. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.2. The mean %RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the analyte is part of the calibration standard, its %RSD value is included in the evaluation.

12.2.4.3. Summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded 15%, and the results of the mean %RSD calculation must be included in the data package.

12.2.4.4. The use of the grand mean approach will lead to greater uncertainty for those analytes for which the %RSD is > 15%. Review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results, to determine if the calibration linearity poses a significant concern.

12.2.4.4.1. If the grand mean approach is not acceptable due to client or project specific requirements, employ one of the other calibration options (see Section 12.2.5.), or adjust instrument operating conditions and/or the calibration range until the %RSD is ≤ 15%.

12.2.5. Other calibration options are as follows:

12.2.5.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.99.

12.2.5.2. The section calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

12.2.5.2.1. This option requires at least six calibration levels.

12.2.6. The relative retention time (RRT) of each analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.7. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.8. The relative retention time (RRT) of each target analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.8.1. The RRT criterion is not a requirement. However, non-compliance should be considered indicative of a problematic calibration for the affected target analytes.

12.2.9. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.9.1. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

12.3.1.1. If the calibration option is average relative response, the %D is the percent difference.

12.3.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.3.2. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 50%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

12.4.2.1. If the calibration option is average relative response, the %D is the percent difference.

12.4.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.4.3. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 50%.

12.4.4. The internal standard responses and retention times for the CCV must be evaluated immediately during or after data acquisition.

12.4.4.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

12.4.4.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

12.4.4.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.5. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Effect corrective action and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, recalibrate or demonstrate acceptable performance with two consecutive CCVs.

12.4.5.1. To demonstrate acceptable performance with two consecutive CCVs, the concentrations of the two CCV standards must be at two different levels within the calibration range. In addition, the concentration of one CCV standard shall be below the mid level.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.2.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.2.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.2.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.2.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.5.2.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.5.3. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-extracted and/or re-analyzed.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), surrogates added to each sample, and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate spike compound recoveries are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same extract should be re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate

recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-extracted and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for internal standard compounds are as follows:

12.6.3.1. The internal standard responses (area counts) for all samples including QC check samples and method blanks must be monitored.

12.6.3.2. If the area count of any internal standard in a sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

12.6.3.2.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

12.6.4. The acceptance criteria for MS/MSDs compounds are as follows:

12.6.4.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Prior to the analysis of sample or QC extracts, the GC/MS system must be hardware tuned and an acceptable multi-point calibration established. The acceptance criteria for the parameters are listed in Sections 12.1. and 12.2.

13.1.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

13.1.2. The spectrometer must produce a mass spectrum that meets all criteria when 50 ng of DFTPP is introduced in GC/MS.

13.1.3. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not background-subtract part of the DFTPP peak.

13.1.4. Benzidine and pentachlorophenol should be present at their normal responses and no peak tailing should be present. If the benzidine and/or pentachlorophenol responses are low or peak tailing exists, effect corrective action and retune/recalibrate prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the analytical column.

13.1.5. 4,4'-DDT is included in the tune solution to check for degradation. The acceptance criteria for degradation of 4,4'-DDT to DDE and DDD is less than or equal to 20%. If 4,4'-DDT degradation exceeds 20%, effect corrective action and re-tune the system prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the guard column.

13.2. Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14. ▶PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Carrier gas flow rate	1 mL/min at 7.15 psi
Initial temperature	40°C, hold 1.50 min
Temperature program	40°C to 280°C at 22.00°C/min 280°C to 310°C at 5.00°C/min
Final temperature	310°C, hold 6.00 min
Transfer line temperature	285°C
Scan range	35~500 amu

14.1.2. Autoinjector is set to inject 1 µL of sample or QC extract.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4.

14.2.1. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

14.2.2. If not, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC/MS sample tray.

14.4. Sample vials are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch)

7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.2. Item 2: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. Only the CCCs and SPCCs are monitored for acceptance. An acceptable CCV is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.3. Item 3: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.4.3.2. One LCS is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6. ***The LCSD is required if MS/MSD are not prepared and analyzed along with field samples.***

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., surrogates, internal standards, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand.

14.4.5.2. An MB is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs may be placed in the sequence.

14.4.5.3. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one

of the instruments. A solvent blank consisting of methylene chloride must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.4.6. Item 6: Up to 20 sample extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrumentation is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.7. Item 7: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof extracted concurrently.

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.6.

14.5. Ensure that a sufficient amount of methylene chloride is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles. Specifically, ensure that the solvent rinse bottles are full and waste bottles are empty at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run log book.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the area count of each internal standard compound in all samples including QC check samples and method blanks.

14.8.1.1. If the area count of any internal standard in the sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

14.8.1.1.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

14.8.2. The qualitative identification of each analyte determined by this method is based on the 1) elution of the sample component at the same relative retention time (RRT) as the standard component and 2) comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum.

14.8.2.1. The reference mass spectrum should be obtained from the GC/MS within the same 12-hour period as the sample analysis.

14.8.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.3. Analytes should be identified as present when the following criteria are met:

14.8.3.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at a compound-specific retention time will be accepted as meeting this criterion.

14.8.3.2. The RRT of the sample analyte is within ±0.06 RRT units of the RRT of the standard analyte.

14.8.3.3. The relative intensities of the characteristic ions agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.8.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.3.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important.

14.8.3.6. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.8.4. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one with the retention time nearest that of a given analyte.

14.8.4.1. If the %RSD of a target analyte's response factor is ≤ 15%, then the concentration in the extract may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating %RSD is listed in Section 15.2.

14.8.4.2. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided below are for the purpose of understanding.

14.8.4.2.1. The concentration of the analyte in an aqueous sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the volume of the aqueous sample extracted. The formula for calculating the concentration is listed in Section 15.8.

14.8.4.2.2. The concentration of the analyte in a solid or oil sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the mass of the solid or oil sample extracted. The formula for calculating the concentration is listed in Section 15.9.

14.8.5. Upon request, a library search may be made for the purpose of tentative identification of compounds not associated with the calibration standards. Refer to the reporting procedure outlined in the current revision of SOP-T025.

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where: RF = response factor for target analyte being measured.

A_x = area of the characteristic ion for target analyte being measured.
C_{is} = concentration of the applicable internal standard.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_x = concentration of target analyte being measured.

Note: Concentrations must be in equivalent units.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the applicable internal standard in mg/L.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample extracted in L.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (or oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in mg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (or oil) sample extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The percent breakdown is calculated as follows:

$$\%B = \frac{A_{degradation}}{A_{total}} \times 100$$

where: %B = percent breakdown of DDT.
$A_{degradation}$ = total degradation peak areas (see Note 1).
A_{total} = total peak areas (see Note 2).

Note 1: The total degradation peak areas are the areas of DDE and DDD for DDT breakdown.

Note 2: The total peak areas are the areas of DDT, DDD, and DDE for DDT breakdown.

15.11. The relative retention time of each target analyte is calculated as follows:

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.
RT_x = retention time of target analyte.
RT_{is} = retention time of the applicable internal standard.

15.12. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for oil, soil, and solid waste samples.

15.12.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.13. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. ►POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS compounds vary depending upon historical data. The lower and upper acceptance limits for %REC of each LCS compound are based upon the historical average recovery ± 3S. All LCS compounds must be within acceptance limits (see Section 12.5.2. for additional information).

18.1.1. If the LCS is above the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only ***prepared and analyzed when required by project QAPP or*** when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for oil, soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If

previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries

of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8270C, USEPA, Revision 3, December 1996.

22.2. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Pre-promulgation Version, Method 8270D, USEPA, Revision 4, February 2006.

22.3. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.4. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.5. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.6. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.7. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

22.8. Semivolatile Organic Compounds (SVOCs), SW-846 Method 8270, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Requirements for Low Level N-Nitrosodimethylamine (NDMA) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.2. Appendix B: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.3. Appendix C: Requirements for Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.4. Appendix D: Additional Quality Control Criteria for Department of Defense Project.

23.5. Appendix E: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) and Phthalates Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode for solid matrices.

24. MODIFICATIONS

Calscience SOP M404 Section	Reference Document EPA Method 8270C Section	Summary of Modification
All	All	None.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.8	SOP Updated.	Y. Patel	11/12/12
	Sec.6: LOD / LOQ definations added. Sec.9 Instrument Software and maintenance reference added. Sec.10 Table of ICAL, ICV and CCV replaced. Sec.11 Samples and extract storage requirements corrected as per method. Sec. 12 Alternate calibration options added for ICAL, ICV and CCV Sec. 24 and 25 created. Appendix A, B, C, D & E updated.		
4.9	Entire document: Update company name and replace EQLs with RLs. Section 6: Update definitions. Sections 8 and 17: Add SDSs. Sections 14 and 18 and appendices: Update LCSD requirement.	L. Hunt	03/09/15

Appendix A

REQUIREMENTS FOR LOW LEVEL N-NITROSODIMETHYLAMINE (NDMA) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level n-nitrosodimethylamine (NDMA) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil/solid matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid

3 µg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard neat compound, in sealed glass ampule, containing 100 mg of NDMA, is used to prepare calibration standards.

5.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of NDMA, 2000 ppm of surrogate, and 1000 ppm of internal standard are used to prepare calibration and check standards.

5.3. Calibration standard solutions containing 1000 ppb of NDMA, 5000 ppb of internal standard, and 1000 ppb of surrogate in methylene chloride are used to prepare calibration standards.

5.3.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppb)				
NDMA	2	10	20	50	100
internal standard	20	20	20	20	20
surrogate	2	10	20	50	100

5.4. The initial calibration verification (ICV) solution contains 20 ppb each of NDMA, internal standard, and surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.5. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppb)
NDMA	20
internal standard	20
surrogate	20

5.6. One CCV solution is used daily.

5.7. Surrogate standard solution containing 1000 ppb of 1,4-dichlorobenzene-d_4 in acetone or methylene chloride.

5.7.1. Add 40 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.8. Spike standard solution containing 1000 ppb of NDMA in acetone or methylene chloride.

5.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.8.2. Add 40 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.9. Internal standard solution containing 1000 ppb of n-nitrosodimethylamine-d_6 in methylene chloride.

5.9.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.10. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.11. All stock standards must be inspected and documented prior to use.

6. SELECTED ION MONITORING (SIM) PARAMETERS

6.1. The MSD will focus on the following selected ions of NDMA.

Analyte	Ions
n-nitrosodimethylamine-d_6	46, 80
n-nitrosodimethylamine	42, 74
1,4-dichlorobenzene-d_4	115, 150, 152

Appendix B

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level polynuclear aromatic hydrocarbons (PAHs) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Aqueous
100 µg/kg	1.0 µg/L

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-N201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 10 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 5:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each PAH target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in methylene chloride are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
PAHs	0.1	0.5	1.0	2.0	5.0
internal standards	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	1.0	2.0	5.0
surrogates	0.1	0.5	1.0	2.0	5.0

5.2.2. The calibration check compounds (CCCs) are acenaphthene, fluoranthene, and benzo(a)pyrene.

5.3. The initial calibration verification (ICV) solution contains 1.0 ppm of each PAH / target analyte, 5.0 ppm of each internal standard, 1.0 ppm of each check compound, and 1.0 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
PAHs	1.0
internal standards	5.0
CCCs	1.0
surrogates	1.0

5.5. One CCV solution is used daily.

5.6. The surrogate standard solution contains 4.0 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14} in acetone or methylene chloride.

5.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.7. Spike standard solution containing 4.0 ppm each of acenaphthene and pyrene in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.7.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.7.2. Add 500 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.8. The internal standard solution contains 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

5.8.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.9. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.10. All stock standards must be inspected and documented prior to use.

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the PAHs.

Analyte	Ions	Retention Time Range
1,4-dichlorobenzene-d_4	150, 152, 115	9.54 to 10.14 min
naphthalene-d_8	136, 68, 108	12.28 to 12.88 min
nitrobenzene-d_5	82, 54, 128	10.82 to 11.42 min
naphthalene	128, 129, 127	12.32 to 12.92 min
2-methylnaphthalene	142, 141, 115	13.98 to 14.58 min
1-methylnaphthalene	142, 141, 115	14.23 to 14.83 min
acenaphthene-d_{10}	164, 162, 80	16.71 to 17.31 min
2-fluorobiphenyl	172, 171, 85	15.02 to 15.62 min
acenaphthylene	152, 151, 76	16.28 to 16.88 min
acenaphthene	153, 154, 76	16.79 to 17.39 min
fluorene	166, 165, 82	18.20 to 18.80 min
phenanthrene-d_{10}	188, 94, 80	20.82 to 21.42 min
phenanthrene	178, 89, 76	20.88 to 21.48 min
anthracene	178, 76, 89	21.01 to 21.61 min

Analyte	Ions	Retention Time Range
fluoranthene	202, 203, 101	24.35 to 24.95 min
chrysene-d_{12}	240, 236, 120	28.59 to 29.19 min
pyrene	202, 200, 101	24.97 to 25.57 min
p-terphenyl-d_{14}	244, 122, 212	25.68 to 26.28 min
benzo(a) anthracene	228, 114, 226	28.54 to 29.14 min
chrysene	228, 114, 226	28.65 to 29.25 min
perylene-d_{12}	264, 132, 260	32.48 to 33.08 min
benzo(b) fluoranthene	252, 253, 126	31.53 to 32.13 min
benzo(k) fluoranthene	252, 253, 126	31.59 to 32.19 min
benzo(a) pyrene	252, 253, 126	32.32 to 32.92 min
indeno(1,2,3-c,d) pyrene	276, 138, 277	35.13 to 35.73 min
dibenz(a,h) anthracene	278, 279, 139	35.24 to 35.84 min
benzo(g,h,i) perylene	276, 138, 277	35.83 to 36.43 min

Appendix C

REQUIREMENTS FOR LOW LEVEL ORGANOCHLORINE PESTCIDIES AND POLYCHLORINATED BIPHENYL (PCB) CONGENERS DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Determination of Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners in Selected Ion Monitoring (SIM) Mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Aqueous
5 µg/kg	0.1 µg/L

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 20 ppm of each pesticide target analyte, 20 ppm of each PCB congener target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each pesticide target analyte (2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, DDMU, and DDNU),

20 ppm of each PCB congener target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in hexane are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
pesticides	0.05	0.5	1.0	2.0	5.0
PCB congeners	0.01	0.05	0.5	1.0	2.0
internal standards	5.0	5.0	5.0	5.0	5.0
surrogates	0.01	0.05	0.5	1.0	2.0

5.2.2. The 1.0-ppm standard is also used as the continuing calibration verification solution.

5.3. The initial calibration verification (ICV) solution contains 1.0 ppm of each pesticide or PCB congener target analyte, 5.0 ppm of each internal standard, and 1.0 ppm of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial five-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
pesticides	1.0
PCB congeners	0.5
internal standards	5.0
surrogates	0.5

5.4.2. One CCV solution is used daily.

5.5. Surrogate standard solution containing 4.0 ppm of p-terphenyl-d_{14} in acetone or methylene chloride.

5.5.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.6. Spike standard solution containing 4.0 ppm of each pesticide or 100 ppm PCB congener in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.6.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

5.6.2. Add 10 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.7. The internal standard solution for pesticide analysis contains 250 ppm of acenaphthene-d_{10} in methylene chloride. The internal standard solution for PCB congener analysis contains 250 ppm each of phenanthrene-d_{10} and chrysene-d_{12} in methylene chloride.

5.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

5.8. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

5.9. All stock standards must be inspected and documented prior to use.

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each analyte is ≤ 30%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each pesticide analyte is ≤ 50%, and the %D for each PCB congener analyte is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the pesticides.

Analyte	Ions	Retention Time
acenaphthene-d_{10}	164, 162, 80	4.088 min
DDNU	178, 248, 213	6.868 min
2,4'-DDE	246, 318, 176	9.049 min
DDMU	212, 282, 176	9.086 min
4,4'-DDE	246, 318, 176	10.088 min
p-terphenyl-d_{14}	244, 122, 212	10.130 min
2,4'-DDD	235, 165, 199	10.629 min
2,4'-DDT	235, 237, 165	11.488 min
4,4'-DDD	235, 237, 165	12.146 min

7.2. The Mass Selective detector will focus on the following selected ions of the PCB congeners.

Analyte	Congener Number	Ions	Retention Time
phenanthrene-d_{10}		188, 94, 80	9.641 min
2,4'-dichlorobiphenyl	8	222, 152	10.021 min
2,2',5-trichlorobiphenyl	18	256, 186	10.268 min
2,4,4'-trichlorobiphenyl	28	256, 186	10.496 min
2,2',5,5'-tetrachlorobiphenyl	52	292, 220	10.792 min
2,2',4,5'-tetrachlorobiphenyl	49	292, 220	10.815 min
2,2',3,5'-tetrachlorobiphenyl	44	292, 220	11.000 min
3,4,4'-trichlorobiphenyl	37	256, 186	11.114 min
2,4,4',5-tetrachlorobiphenyl	74	292, 220	11.301 min
2,3',4',5-tetrachlorobiphenyl	70	292, 220	11.380 min
2,3',4,4'-tetrachlorobiphenyl	66	292, 220	11.406 min
2,2',4,5,5'-pentachlorobiphenyl	101	326, 254	11.564 min
2,2',4,4',5-pentachlorobiphenyl	99	326, 254	11.604 min
2,3',4,4',6-pentachlorobiphenyl	119	326, 254	11.681 min
2,2',3,4,5'-pentachlorobiphenyl	87	326, 254	11.810 min
p-terphenyl-d_{14}		244, 122, 212	11.819 min
3,4,4',5-tetrachlorobiphenyl	81	292, 220	11.877 min
2,3,3',4',6-pentachlorobiphenyl	110	326, 254	11.913 min
2,2',3,5,5',6-hexachlorobiphenyl	151	360, 290	11.948 min
3,3',4,4'-tetrachlorobiphenyl	77	292, 220	12.000 min
2,2',3,4',5',6-hexachlorobiphenyl	149	360, 290	12.066 min
2,3',4,4',5'-pentachlorobiphenyl	123	326, 254	12.115 min
2,3',4,4',5-pentachlorobiphenyl	118	326, 254	12.150 min
2,3,4,4',5-pentachlorobiphenyl	114	326, 254	12.200 min
2,2',3,4,4',6,6'-heptachlorobiphenyl	184	394, 324	12.206 min
2,2',4,4',5,5'-hexachlorobiphenyl	153	360, 290	12.296 min
2,3',4,4',5',6-hexachlorobiphenyl	168	360, 290	12.330 min
2,3,3',4,4'-pentachlorobiphenyl	105	326, 254	12.387 min
2,2',3,4,4',5'-hexachlorobiphenyl	138	360, 290	12.536 min
2,3,3',4,4',6-hexachlorobiphenyl	158	360, 290	12.558 min
2,2',3,4',5,5',6-heptachlorobiphenyl	187	394, 324	12.632 min
2,2',3,4,4',5',6-heptachlorobiphenyl	183	394, 324	12.672 min
3,3',4,4',5-pentachlorobiphenyl	126	326, 254	12.704 min
2,2',3,3',4,4'-hexachlorobiphenyl	128	360, 290	12.794 min

Analyte	Congener Number	Ions	Retention Time
2,3',4,4',5,5'-hexachlorobiphenyl	167	360, 290	12.824 min
2,2',3,3',4,5',6'-heptachlorobiphenyl	177	394, 324	12.892 min
2,3,3',4,4',5-hexachlorobiphenyl	156	360, 290	13.022 min
2,3,3',4,4',5'-hexachlorobiphenyl	157	360, 290	13.087 min
2,2',3,4,4',5,5'-heptachlorobiphenyl	180	394, 324	13.138 min
chrysene-d_{12}		240, 236, 120	13.253 min
2,2',3,3',4,4',5-heptachlorobiphenyl	170	394, 324	13.433 min
2,2',3,3',4,5',6,6'-octachlorobiphenyl	201	430, 358	13.463 min
3,3',4,4',5,5'-hexachlorobiphenyl	169	360, 290	13.464 min
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	394, 324	13.790 min
2,2',3,3',4,4',5,6-octachlorobiphenyl	195	430, 358	13.828 min
2,2',3,3',4,4',5,5'-octachlorobiphenyl	194	430, 358	14.125 min
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	464, 196	14.486 min
decachlorobiphenyl	209	428, 358	14.741 min

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for DoD Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solution contains 1000 ppm of each target analyte in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

3.1.1. The standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

3.1.2. Add 200 µL of the spike standard to each MS/MSD and LCS sample prior to extraction.

3.1.3. The spike standard solution contains all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

4.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

4.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. No samples shall be analyzed without a valid LOD.

4.2. Limit of Quantitation (LOQ)

4.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.3. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

4.3. Tuning

4.3.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

4.3.2. Benzidine and pentachlorophenol should be present at their normal responses and should not exceed a tailing factor of 2.

4.4. Initial Calibration

4.4.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

4.4.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

4.4.3. If these criteria are not met ,other calibration options are as follows:

4.4.3.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.995.

4.4.3.2. The section calibration option is non-linear quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

4.4.3.2.1. This option requires at least six calibration levels for second order and seven levels for third order.

4.4.4. The relative retention time (RRT) of each target analyte in each calibration standard must be within ± 0.06 RRT units.

4.4.5. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

4.5. Initial Calibration Verification (ICV)

4.5.1. The initial calibration is deemed valid if the %D for each project analyte is ≤ 20%.

4.5.1.1. If the calibration option is average relative response, the %D is the percent difference.

4.5.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.5.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

4.6. Continuing Calibration Verification (CCV)

4.6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis.

4.6.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

4.6.2.1. If the calibration option is average relative response, the %D is the percent difference.

4.6.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.7. Retention Time Window

4.7.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

4.7.1.1. Absolute retention time window for each analyte, surrogate, or internal standard is the retention time of the respective analyte, surrogate, or internal standard in the midpoint calibration standard ± 30 seconds.

4.7.1.2. Document the serial number of the analytical column associated with the retention time window.

4.8. Internal Standard Verification

4.8.1. The internal standard responses and retention times for all standards and samples must be evaluated.

4.8.1.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

4.8.1.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

4.8.1.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

4.8.1.4. If corrective action fails in a sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

4.9. Event Based Quality Control (LCSs and MBs)

4.9.1. Laboratory Control Samples (LCSs)

4.9.1.1. The lower and upper acceptance limits for %REC of each LCS compound in aqueous matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	50	105	40	115
Anthracene	55	110	45	120
Benzo(a)anthracene	55	110	45	120
Benzo(a)pyrene	55	110	45	120
Benzo(b)fluoranthene	45	120	35	130
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	135
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	30	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	120
Indeno(1,2,3-c,d)pyrene	45	125	30	140
Naphthalene	40	100	30	115
Phenanthrene	50	115	40	130
Pyrene	50	130	35	140
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	50	115	40	125
2,4-Dichlorophenol	50	105	40	115
2,4-Dimethylphenol	30	110	15	125
2,4-Dinitrophenol	15	140	10	160
2-Chlorophenol	35	105	25	115
2-Methylphenol	40	110	25	120
2-Nitrophenol	40	115	25	125
3-Methylphenol / 4-Methylphenol	30	110	20	125
4,6-Dinitro-2-methylphenol	40	130	25	145
4-Chloro-3-methylphenol	45	110	35	120
4-Nitrophenol	0	125	0	145
Pentachlorophenol	40	115	25	130
Phenol	0	115	0	135
Benzoic acid	0	125	0	150
Basic				
3,3'-Dichlorobenzidine	20	110	10	125
4-Chloroaniline	15	110	10	125

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	40	125	30	140
Butyl benzyl phthalate	45	115	35	130
Di-n-butyl phthalate	55	115	45	125
Di-n-octyl phthalate	35	135	20	155
Diethyl phthalate	40	120	30	130
Dimethyl phthalate	25	125	10	145
Nitrosoamines				
N-Nitrosodi-n-propylamine	35	130	20	145
N-Nitrosodimethylamine	25	110	10	125
N-Nitrosodiphenylamine	50	110	35	120
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	105	35	115
Bis(2-chloroethyl)ether	35	110	25	120
Bis(2-chloroisopropyl)ether	25	130	10	150
Hexachloro-1,3-butadiene	25	105	15	115
Hexachloroethane	30	95	15	105
Halogenated Aromatics				
1,2,4-Trichlorobenzene	35	105	25	120
1,2-Dichlorobenzene	35	100	20	115
1,3-Dichlorobenzene	30	100	20	110
1,4-Dichlorobenzene	30	100	20	110
2-Chloronaphthalene	50	105	40	115
4-Bromophenyl phenyl ether	50	115	40	125
4-Chlorophenyl phenyl ether	50	110	40	120
Hexachlorobenzene	50	110	40	120
Nitroaromatics				
2,4-Dinitrotoluene	50	120	40	130
2,6-Dinitrotoluene	50	115	35	130
2-Nitroaniline	50	115	35	125
3-Nitroaniline	20	125	10	145
4-Nitroaniline	35	120	20	130
Nitrobenzene	45	110	35	120
Neutral Aromatics				
Carbazole	50	115	35	130
Dibenzofuran	55	105	45	115
Others				
1,2-Diphenylhydrazine	55	115	45	120
Benzyl alcohol	30	110	15	125
Isophorone	50	110	40	125

4.9.1.2. The lower and upper acceptance limits for %REC of each LCS compound in solid matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	45	105	35	115
Anthracene	55	105	45	115
Benzo(a)anthracene	50	110	40	120
Benzo(a)pyrene	50	110	40	120
Benzo(b)fluoranthene	45	115	35	125
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	140
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	25	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	115
Indeno(1,2,3-c,d)pyrene	40	120	25	135
Naphthalene	40	105	30	120
Phenanthrene	50	110	40	120
Pyrene	45	125	35	135
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	45	110	30	120
2,4-Dichlorophenol	45	110	35	120
2,4-Dimethylphenol	30	105	20	115
2,4-Dinitrophenol	15	130	10	150
2-Chlorophenol	45	105	35	115
2-Methylphenol	40	105	30	115
2-Nitrophenol	40	110	30	120
3-Methylphenol / 4-Methylphenol	40	105	30	120
4,6-Dinitro-2-methylphenol	30	135	10	155
4-Chloro-3-methylphenol	45	115	35	125
4-Nitrophenol	15	140	10	160
Pentachlorophenol	25	120	10	135
Phenol	40	100	30	110
Benzoic acid	0	110	0	130
Basic				
3,3'-Dichlorobenzidine	10	130	0	145
4-Chloroaniline	10	95	0	110
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	45	125	35	140
Butyl benzyl phthalate	50	125	35	135
Di-n-butyl phthalate	55	110	45	120
Di-n-octyl phthalate	40	130	25	145
Diethyl phthalate	50	115	40	125
Dimethyl phthalate	50	110	40	120
Nitrosoamines				
N-Nitrosodi-n-propylamine	40	115	30	125
N-Nitrosodimethylamine	20	115	10	130

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Nitrosoamines				
N-Nitrosodiphenylamine	50	115	40	125
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	110	30	120
Bis(2-chloroethyl)ether	40	105	25	115
Bis(2-chloroisopropyl)ether	20	115	10	130
Hexachloro-1,3-butadiene	40	115	25	130
Hexachloroethane	35	110	20	120
Halogenated Aromatics				
1,2,4-Trichlorobenzene	45	110	30	120
1,2-Dichlorobenzene	45	95	35	105
1,3-Dichlorobenzene	40	100	30	110
1,4-Dichlorobenzene	35	105	25	115
2-Chloronaphthalene	45	105	35	115
4-Bromophenyl phenyl ether	45	115	35	130
4-Chlorophenyl phenyl ether	45	110	35	120
Hexachlorobenzene	45	120	35	130
Nitroaromatics				
2,4-Dinitrotoluene	50	115	35	130
2,6-Dinitrotoluene	50	110	35	125
2-Nitroaniline	45	120	30	130
3-Nitroaniline	25	110	15	125
4-Nitroaniline	35	115	20	125
Nitrobenzene	40	115	30	125
Neutral Aromatics				
Carbazole	45	115	30	130
Dibenzofuran	50	105	40	110
Others				
Benzyl alcohol	20	125	10	140
Isophorone	45	110	30	125

4.9.2. Method Blanks (MBs)

4.9.2.1. The concentration of a target analyte in an MB should be ≤ ½ RL. The concentrations of common laboratory contaminants should be < RL.

4.9.2.2. If these criteria are not met, investigate and eliminate the source of contamination.

4.9.2.3. Determine whether to reprocess the samples associated with the failed MB based on the following checks:

4.9.2.3.1. The concentration of a target analyte in the MB is ≥ RL as established by the test method or by regulation, and is > 1/10 of the amount measured in any sample.

4.9.2.3.2. The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.

4.9.2.4. Any sample that meets either one or both of the checks described in Section 4.6.2.3. shall be reprocessed in a subsequent preparatory batch, except when the sample analysis resulted in a non-detect.

4.9.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.10. Matrix Based Quality Control (Surrogates and MS/MSDs)

4.10.1. Surrogates

4.10.1.1. The lower and upper acceptance limits for %REC of each surrogate spike compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	50	110
Terphenyl-d_{14}	50	135
2,4,6-Tribromophenol	40	125
2-Fluorophenol	20	110
Phenol-d_5 / Phenol-d_6	10	115
Nitrobenzene-d_5	40	110

4.10.1.2. The lower and upper acceptance limits for %REC of each surrogate spike compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	45	105
Terphenyl-d_{14}	30	125
2,4,6-Tribromophenol	35	125
2-Fluorophenol	35	105
Phenol-d_5 / Phenol-d_6	40	100
Nitrobenzene-d_5	35	100

4.10.2. Matrix Spikes (MS/MSDs)

4.10.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	50	105
Anthracene	55	110
Benzo(a)anthracene	55	110
Benzo(a)pyrene	55	110
Benzo(b)fluoranthene	45	120
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	45	125
Naphthalene	40	100
Phenanthrene	50	115
Pyrene	50	130
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	50	115
2,4-Dichlorophenol	50	105
2,4-Dimethylphenol	30	110
2,4-Dinitrophenol	15	140
2-Chlorophenol	35	105
2-Methylphenol	40	110
2-Nitrophenol	40	115
3-Methylphenol / 4-Methylphenol	30	110
4,6-Dinitro-2-methylphenol	40	130
4-Chloro-3-methylphenol	45	110
4-Nitrophenol	0	125
Pentachlorophenol	40	115
Phenol	0	115
Benzoic acid	0	125
Basic		
3,3'-Dichlorobenzidine	20	110
4-Chloroaniline	15	110
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	40	125
Butyl benzyl phthalate	45	115
Di-n-butyl phthalate	55	115
Di-n-octyl phthalate	35	135
Diethyl phthalate	40	120
Dimethyl phthalate	25	125
Nitrosoamines		
N-Nitrosodi-n-propylamine	35	130
N-Nitrosodimethylamine	25	110

Analyte	Control Limit	
	Lower	Upper
Nitrosoamines		
N-Nitrosodiphenylamine	50	110
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	105
Bis(2-chloroethyl)ether	35	110
Bis(2-chloroisopropyl)ether	25	130
Hexachloro-1,3-butadiene	25	105
Hexachloroethane	30	95
Halogenated Aromatics		
1,2,4-Trichlorobenzene	35	105
1,2-Dichlorobenzene	35	100
1,3-Dichlorobenzene	30	100
1,4-Dichlorobenzene	30	100
2-Chloronaphthalene	50	105
4-Bromophenyl phenyl ether	50	115
4-Chlorophenyl phenyl ether	50	110
Hexachlorobenzene	50	110
Nitroaromatics		
2,4-Dinitrotoluene	50	120
2,6-Dinitrotoluene	50	115
2-Nitroaniline	50	115
3-Nitroaniline	20	125
4-Nitroaniline	35	120
Nitrobenzene	45	110
Neutral Aromatics		
Carbazole	50	115
Dibenzofuran	55	105
Others		
1,2-Diphenylhydrazine	55	115
Benzyl alcohol	30	110
Isophorone	50	110

4.10.2.2. The lower and upper acceptance limits for %REC of each MS/MSD compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	45	105
Anthracene	55	105
Benzo(a)anthracene	50	110
Benzo(a)pyrene	50	110
Benzo(b)fluoranthene	45	115
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	40	120
Naphthalene	40	105
Phenanthrene	50	110
Pyrene	45	125
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	45	110
2,4-Dichlorophenol	45	110
2,4-Dimethylphenol	30	105
2,4-Dinitrophenol	15	130
2-Chlorophenol	45	105
2-Methylphenol	40	105
2-Nitrophenol	40	110
3-Methylphenol / 4-Methylphenol	40	105
4,6-Dinitro-2-methylphenol	30	135
4-Chloro-3-methylphenol	45	115
4-Nitrophenol	15	140
Pentachlorophenol	25	120
Phenol	40	100
Benzoic acid	0	110
Basic		
3,3'-Dichlorobenzidine	10	130
4-Chloroaniline	10	95
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	45	125
Butyl benzyl phthalate	50	125
Di-n-butyl phthalate	55	110
Di-n-octyl phthalate	40	130
Diethyl phthalate	50	115
Dimethyl phthalate	50	110
Nitrosoamines		
N-Nitrosodi-n-propylamine	40	115
N-Nitrosodimethylamine	20	115
N-Nitrosodiphenylamine	50	115
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	110
Bis(2-chloroethyl)ether	40	105
Bis(2-chloroisopropyl)ether	20	115
Hexachloro-1,3-butadiene	40	115
Hexachloroethane	35	110
Halogenated Aromatics		
1,2,4-Trichlorobenzene	45	110

Analyte	Control Limit	
	Lower	Upper
Halogenated Aromatics		
1,2-Dichlorobenzene	45	95
1,3-Dichlorobenzene	40	100
1,4-Dichlorobenzene	35	105
2-Chloronaphthalene	45	105
4-Bromophenyl phenyl ether	45	115
4-Chlorophenyl phenyl ether	45	110
Hexachlorobenzene	45	120
Nitroaromatics		
2,4-Dinitrotoluene	50	115
2,6-Dinitrotoluene	50	110
2-Nitroaniline	45	120
3-Nitroaniline	25	110
4-Nitroaniline	35	115
Nitrobenzene	40	115
Neutral Aromatics		
Carbazole	45	115
Dibenzofuran	50	105
Others		
Benzyl alcohol	20	125
Isophorone	45	110

4.10.2.3. The RPD between the MS/MSD compounds is ≤ 30%.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix E

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND PTHTHALATES DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE FOR SOLID MATRICES

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level polynuclear aromatic hydrocarbons (PAHs) and Phthalates determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode for solid matrices.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil/solid matrices.

3. DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solids

2–10 µg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

4.2.

Type of Sample Preparation	EPA Method No.	SOP No.
Pressurized Fluid Extraction	3545A	SOP-M204

4.3. The initial sample aliquot mass for soil/solid sample is 100 g.

4.3.1. The final extract volume at the completion of the concentration step is 2 mL.

4.3.2. The resulting preparation factor for soil/solid sample is 50:1.

5. PROCEDURE MODIFICATIONS FOR LOW LEVEL REPORTING IN SOLID MATRICES

5.1. Sample Preparation

5.1.1. Utilizing SOP M204 "EPA Method 3545, Pressurized Fluid Extraction (PFE)" the sample weight and final extract volume are modified as follows:

5.1.2. Sample weight: Increased from 20 g to 100g

5.1.3. Final extract volume: No change, remains 2 mL.

6. STANDARDS

6.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH / phthalate target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

6.2. Calibration standard solutions containing 200 ppm of each PAH / phthalate target analyte, 2000 ppm of each internal standard and 200 ppm of each surrogate in methylene chloride are used to prepare calibration standards.

6.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)						
PAHs / Phthalates	0.1	0.5	5.0	8.0	10.0	15.0	20.0
internal standards	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	5.0	8.0	10.0	15.0	20.0
surrogates	0.1	0.5	5.0	8.0	10.0	15.0	20.0

6.2.2. The calibration check compounds (CCCs) are acenaphthene, fluoranthene, benzo(a)pyrene, and di-n-octyl phthalate.

6.3. The initial calibration verification (ICV) solution contains 10 ppm of each PAH / phthalate target analyte, 5.0 ppm of each internal standard, 10 ppm of each check compound, and 10 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

6.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

6.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
PAHs / Phthalates	10.0
internal standards	5.0
CCCs	10.0
surrogates	10.0

6.5. One CCV solution is used daily.

6.6. The surrogate standard solution contains 400 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl and p-terphenyl-d_{14} in acetone or methylene chloride.

6.6.1. Add 50 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

6.7. The spike standard solution contains 200 ppm each of PAHs and phthalates in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

6.7.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

6.7.2. Add 100 µL of the spike standard to each MS/MSD and LCS sample prior to extraction.

6.8. The internal standard solution contains 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10} and perylene-d_{12} in methylene chloride.

6.8.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

6.9. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

6.10. All stock standards must be inspected and documented prior to use.

7. QUALITY CONTROL

7.1. Initial Calibration (IC)

7.1.1. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.

7.2. Initial Calibration Verification (ICV)

7.2.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

7.3. Continuing Calibration Verification (CCV)

7.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

8. SELECTED ION MONITORING (SIM) PARAMETERS

8.1. The Mass Selective detector will focus on the following selected ions of the PAHs and Phthalates.

Analyte	Ions	Retention Time Range (min)
naphthalene-d_8	136,68	6.11 to 6.45
nitrobenzene-d_5	82, 54,128	5.38 to 5.49
naphthalene	128, 129, 127	6.09 to 6.49
2-methylnaphthalene	142, 141	6.92 to 7.12
1-methylnaphthalene	142, 141	7.04 to 7.37
acenaphthene-d_{10}	164, 162, 160	8.01 to 8.39
2-fluorobiphenyl	172, 171	7.29 to 7.62
acenaphthylene	152, 151, 153	7.86 to 8.18
acenaphthene	153, 154, 152	8.12 to 8.35
fluorene	166, 165, 167	8.59 to 8.99
phenanthrene-d_{10}	188, 94, 80	9.69 to 9.95
phenanthrene	178, 176, 179	9.69 to9.91
anthracene	178, 176, 179	9.82 to 10.05
fluoranthene	202, 203, 101	11.01 to 11.34
chrysene-d_{12}	240, 236, 120	12.70 to 13.02
pyrene	202, 200, 203	11.25 to 11.60
p-terphenyl-d_{14}	244, 122, 212	11.95 to 11.76
benzo(a) anthracene	228, 229, 226	12.64 to 12.86
chrysene	228, 229, 226	12.79 to 13.11
perylene-d_{12}	264, 265, 260	14.78 to 15.38
benzo(b) fluoranthene	252, 253, 125	14.27 to 14.99
benzo(k) fluoranthene	252, 253, 125	14.41 to 14.61
benzo(a) pyrene	252, 253, 125	14.84 to 15.16
indeno(1,2,3-c,d) pyrene	276, 138, 277	17.02 to 17.19
dibenz(a,h) anthracene	278, 279, 139	16.99 to 17.35
benzo(g,h,i) perylene	276, 138, 277	17.50 to 17.84
Dimethyl phthalate	163, 164, 194	7.79 to 8.13
Diethy phthalate	149, 177, 150	8.60 to 8.85
di-n-butyl phthalate	149, 150, 104	10.34 to 10.71
Butyl benzyl phthalate	149, 91, 206	12.02 to 12.34
bis(2-Ethyl hexyl) phthalate	149, 279, 167	12.79 to 13.15
di-n-octyl phthalate	149, 279, 150	13.70 to 14.04

Title : **SM 2130B, TURBIDITY (NEPHELOMETRIC)**

Document No. : SOP-M770
Revision No. : 0.0
Supersedes : M725, rev. 4.0

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PROPRIETARY INFORMATION STATEMENT

APPROVED FOR RELEASE BY: R Lane — **MANAGEMENT** — 07/08/03 **DATE**

M/Ch — **QA DEPARTMENT** — 07/07/03 **DATE**

1. METHOD IDENTIFICATION

1.1. Turbidity, SM 2130B Nephelometric Method.

2. APPLICABLE MATRICES

2.1. This method may be applied to drinking water, surface water and saline water.

3. DETECTION LIMITS

3.1. This method may be used to report turbidity in the range from 0 to 1000 nephelometric turbidity units (NTUs).

3.2. Higher values may be determined through dilution of the sample prior to measurement.

3.2.1. See Calculations for determination of turbidity concentrations in diluted samples.

3.2.2. Drinking waters with turbidity concentrations greater than 40 NTUs MUST be diluted such that measured concentrations are ≤40 NTUs.

3.2.3. NOTE: The published methods indicate a measurable range of 0 to 40 NTUs, however, advances in instrumentation allow for measurements to 1000 NTUs.

4. SCOPE AND APPLICATION

4.1. Turbidity is an expression of the optical properties that cause light to be scattered or absorbed through a liquid sample and is largely a function of the refractive index, the size and shape of the particles suspended in the solution. As a result, turbidimeters do not produce an "absolute" measurement, but one that is "relative" to the optical nature of the solids suspended in a solution. The turbidimeter provides a linear display of turbidity in nephelometric turbidity units (NTUs).

4.2. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. The method is based upon a comparison, under defined conditions, of the intensity of light scattered by a sample with the intensity of light scattered by a primary reference suspension. The higher the intensity of scattered light, the higher the turbidity.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.10. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.11. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.12. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.13. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.14. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.15. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.16. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.17. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.18. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.19. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.20. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. INTERFERENCES

7.1. Cuvettes must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched.

7.2. The presence of true color, that is the color of water due to dissolved substances that absorb light, will cause the turbidities to be low.

7.3. The presence of floating debris and coarse sediments that settle out rapidly will yield low readings.

7.4. The presence of finely divided air bubbles will affect the results in a positive manner.

7.5. All solutions should be at ambient temperature prior to using the solutions to prevent fogging of the cuvette.

7.6. Do not mix, shake, or agitate the standards. They are ready to use.

7.7. Always use clean glassware and handle cuvettes so there are no fingerprints in the area where light passes through the sample.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, safety glasses and lab coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. APPARATUS AND MATERIALS

9.1. Turbidimeter: HF scientific inc., Micro 100, or equivalent, capable of reading 0.00 to 1000 NTU.

9.2. Sample cuvettes: Glass, 30-ml, reusable.

9.3. Volumetric pipets: 1-25ml, Class A.

9.4. Volumetric flasks: 50-250ml, Class A.

9.5. Wipes: Lint-free cloth, Kimwipe or equivalent.

10. REAGENTS AND STANDARDS

10.1. Secondary turbidity standards: 0.02, 10.0 and 1000 NTU suspensions, obtained from the manufacturer.
10.1.1. Resolution: 0.01 NTU Range = 0.00 – 9.99 NTU
10.1.2. Resolution: 0.1 NTU Range = 10.0 – 99.9 NTU
10.1.3. Resolution: 1 NTU Range = 100 – 1000 NTU

10.2. Formazin stock solution: 4000 NTU suspension, obtained from the manufacturer or another reliable commercial source.

10.3. Reagent water: Turbidity-free water (≤0.02 NTU).

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Samples should be collected in glass containers with Teflon-lined caps, or HDPE containers. There should be minimal headspace in the containers. An amount of 250 mls of sample should be sufficient.

11.2. All samples should be stored in the dark at >0°C - ≤6°C, and without further preservation from the time of collection until analysis.

11.3. Samples should be analyzed within 48 hours from collection.

11.4. Additional sample quantities may be required for QC purposes.

11.5. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standard (LCS) that the measurement system is operating within predetermined control criteria.

12.2. All quality control data should be maintained and available for easy reference and inspection.

12.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 must be followed, unless superseded in this document.

12.4. Calibration of the turbidimeter using formazin shall be performed once every three months or sooner when secondary turbidity standards fail.

12.5. The secondary turbidity standards used in this method have specific turbidities. If the turbidity of the standard falls outside of the applicable acceptance limits, the instrument should be recalibrated.

Secondary Turbidity Standard Acceptance Limits (NTU)

1000	1000 ± 10
10.0	10.0 ± 0.1
0.02	0.02 ± 0.02

12.6. A sample duplicate shall be analyzed for every batch of 20 samples or every 24 hours, whichever is more frequent. The relative percent difference (RPD) between the original and duplicate result shall not exceed 25%. If the percent difference is greater than 25%, halt analysis, effect corrective action and recheck calibration.

12.7. A laboratory control sample (LCS) shall be analyzed for every analytical batch of 20 samples or every 24 hours, whichever is more frequent. The LCS shall consist of a 100 NTU formazin suspension prepared each analytical day by pipetting 2.5 ml of the 4000 NTU formazin suspension into a 100 ml volumetric flask and diluting to volume with reagent water. The recovery of the LCS shall not differ from the expected value by more than 5% (95-105 NTU). If the percent difference (%D) is greater than 5%, halt analysis, effect corrective action and recheck calibration.

13. CALIBRATION AND STANDARDIZATION

13.1. CALIBRATION USING PRIMARY STANDARD (FORMAZIN)

13.1.1. Prepare 1000, 10 and 0.02 NTU (Standard-1, -2 and –3, respectively) calibration standards from the 4000 NTU formazin stock solution (10.2). Shake the stock suspension well before drawing the aliquot that will be used for the calibration standard.

13.1.2. If not already on, depress the ON/OFF key and allow the instrument to warm up for a minimum of 30 minutes.

13.1.3. Press the CAL key.

13.1.4. Pour the 1000 NTU calibration standard into the cuvette. Wipe the outside of the 1000 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.1.5. Place the 1000 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.1.6. Allow the reading to stabilize then press the ◄┘ key.

13.1.7. Pour out the standard and rinse the cuvette three times with reagent water.

13.1.8. Pour the 10 NTU calibration standard into the cuvette. Wipe the outside of the 10.0 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.1.9. Place the 10.0 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.1.10. Allow the reading to stabilize then press the ◄┘ key.

13.1.11. Pour out the 10 NTU standard and rinse the cuvette three times with reagent water.

13.1.12. Pour the 0.02 NTU standard into the cuvette. Wipe the outside of the 0.02 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.1.13. Place the 0.02 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.1.14. Allow the reading to stabilize then press the ◄┘ key.

13.1.15. Pour out the 0.02 NTU standard and rinse the cuvette with reagent water.

13.2. *VERIFICATION OF THE SECONDARY TURBIDITY STANDARDS*

13.2.1. After calibration of the instrument with formazin, verify secondary turbidity standards.

13.2.2. Wipe the outside of the 1000 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.2.3. Place the 1000 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.2.4. Allow the reading to stabilize then press the ◄┘ key. Record the reading in the Turbidity logbook under Standard Value, and on the light shield cap.

13.2.5. Wipe the outside of the 10.0 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.2.6. Place the 10.0 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.2.7. Allow the reading to stabilize then press the ◄┘ key. Record the reading in the Turbidity logbook under Standard Value, and on the light shield cap.

13.2.8. Wipe the outside of the 0.02 NTU calibration standard cuvette with a lint-free wipe. If necessary, use a lens cleaner to remove fingerprints.

13.2.9. Place the 0.02 NTU calibration standard cuvette into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.2.10. Allow the reading to stabilize then press the ◄┘ key. Record the reading in the Turbidity logbook under Standard Value, and on the light shield cap.

13.3. *DAILY CHECK OF SECONDARY TURBIDITY STANDARDS*

13.3.1. If not already on, depress the ON/OFF key and allow the instrument to warm up for a minimum of 30 minutes.

13.3.2. Wipe the outside of the 1000 NTU calibration standard cuvette and place into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.3.3. Allow the reading to stabilize then press the ◄┘ key.

13.3.4. Record the reading in the Turbidity logbook and apply the Standard Turbidity Acceptance Limits (12.5).

13.3.5. Wipe the outside of the 10.0 NTU calibration standard cuvette and place into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.3.6. Allow the reading to stabilize then press the ◄┘ key.

13.3.7. Record the reading in the Turbidity logbook and apply the Standard Turbidity Acceptance Limits (12.5).

13.3.8. Wipe the outside of the 0.02 NTU calibration standard cuvette and place into the optical well. Align the cuvette-indexing notch to the white indexing pin on the turbidimeter.

13.3.9. Allow the reading to stabilize then press the ◄┘ key.

13.3.10. Record the reading in the Turbidity logbook and apply the Standard Turbidity Acceptance Limits (12.5).

13.3.11. If standard readings fall within acceptance limits proceed to Sample Analysis (14.2). However, if standard readings are NOT within acceptance limits, then recalibrate the instrument using formazin.

14. PROCEDURE

14.1. CUVETTE INDEXING

14.1.1. The EPA recommends that cuvettes used for instrument calibration, standardization or sample measurement be indexed. Indexing a cuvette will allow for accurate measurements in the low range by ensuring that the orientation of the cuvette will be identical each time that it is placed in the instrument.

14.1.2. All cuvettes shall be indexed prior to use as follows:

14.1.2.1. Switch ON the turbidimeter and allow to warm up for a minimum of 30 minutes.

14.1.2.2. Inspect the cuvette for scratches in the light path. The critical measuring area is a 3/4" band beginning from approximately 1/2" from bottom of the cuvette. If a scratch(es) is noticed in the light path, the cuvette shall not be used and disposed.

14.1.2.3. Attach the light shield cap to the cuvette; wipe the outside of the cuvette with a lint-free wipe. Alcohol may be used to facilitate cleaning.

14.1.2.4. Place the cuvette into the optical well of the turbidimeter and slowly rotate at least one complete revolution while observing the reading. Locate the position of the lowest reading.

14.1.2.5. Index the cuvette by placing the indexing ring over the cap. Be sure to align the notch on the ring directly adjacent to the white indexing pin on the instrument.

14.1.2.6. The cuvette is now indexed and must remain as a set together with the cap. If the cap is interchanged, the cuvette must be re-indexed.

NOTE: The indexed cuvette is only useable with the turbidimeter to which it has been indexed.

14.2. SAMPLE ANALYSIS

14.2.1. Although the turbidimeter is designed to compensate for temperature, allow the sample to equilibrate to room temperature prior to beginning analysis. This will prevent measurement errors caused by fogging of the cuvette.

14.2.2. Thoroughly shake the sample to suspend any particles that may have settled in storage. Tap sides to release any trapped air bubbles.

14.2.3. Fill the cuvette with the sample. Minimize bubbles by pouring onto the inside wall of the cuvette. Affix cap.

14.2.4. Wipe the outside of the cuvette with a lint-free wipe. (If necessary, use a lens cleaner to remove fingerprints.) Place the cuvette into the optical well of the turbidimeter, and align the indexing notch on the light shielding cap to the white indexing pin on the turbidimeter.

14.2.5. Allow the reading to stabilize then press the ◄┘ key. Record the reading in the Turbidity logbook. Note: Readings should be taken without delay before turbid particles settle.

14.2.6. If the sample turbidity exceeds 1000 NTU, dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 1000 units. Read and record the turbidity and dilution factor.

14.2.7. Dispose of the spent sample and then clean cuvette by rinsing three times with DI water.

14.2.7.1. Rinse sample cuvette by filling ⅔ full using DI water. Cap the cuvette and invert at least five times to remove any possible particulates remaining in the cuvette.

14.2.7.2. Repeat step 14.2.7.1 two more times.

15. CALCULATIONS

15.1. For samples not requiring dilution (≤1000 NTU), the turbidity is read directly from the instrument. No calculations are necessary.

15.2. For samples requiring dilution (>1000 NTU), the turbidity of the original sample is computed as follows:

$$C_S = C_D \times D$$

where:
C_S = Concentration of the sample
C_D = Concentration of the diluted sample solution
D = Dilution factor (final vol./initial vol.)

15.3. The relative percent difference (RPD) is calculated as follows:

$$\%RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:
%RPD = Relative percent difference
C_1 = Original sample concentration
C_2 = Duplicate sample concentration

Note: Concentrations must be in equivalent units

15.4. The percent difference (%D) is calculated as follows:

$$\%D = \frac{(C_T - C_M)}{C_T} \times 100$$

where: %D = Percent difference
C_T = Expected standard concentration
C_M = Measured standard concentration

Note: Concentrations must be in equivalent units

15.5. Reporting limits are listed below. If a dilution was made, multiply the highest reporting limit (1) by the dilution factor.

NTU	Reporting Limit
0.00 - 1.0	0.05
1.1 - 10.0	0.1
10.1 - 100	1
101 - 1000	10
>1000	100

15.6. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. None.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air-purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Additional information regarding internal quality control checks is provided in SOP-T020.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

19.5.1. The analyst must immediately inform the Group Leader of all out of control situations for specific handling instructions.

19.5.2. Event must be documented in detail on an "Out of Control Corrective Action" form and reviewed by the Group Leader. The Group Leader shall implement corrective action, list the specific procedures employed and their outcome on the corrective action form.

19.5.3. A copy of the completed Out of Control Corrective Action form must be included with all affected data packages.

19.5.4. The Group Leader should consult with the Technical Manager and/or Quality Control Manager regarding procedural inquiries and recommendations for method modification.

19.5.5. Management and the QA department as documented in a revised SOP approve modifications to the analytical process.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws.

In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

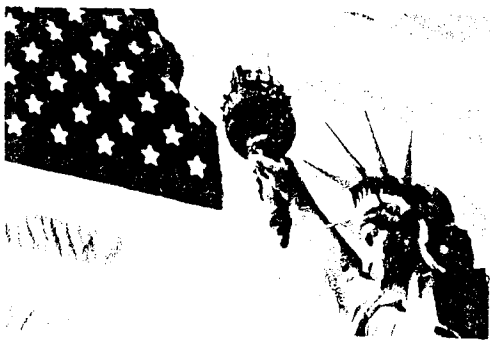
22.1. "2130B Turbidity, Nephelometric Method," Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

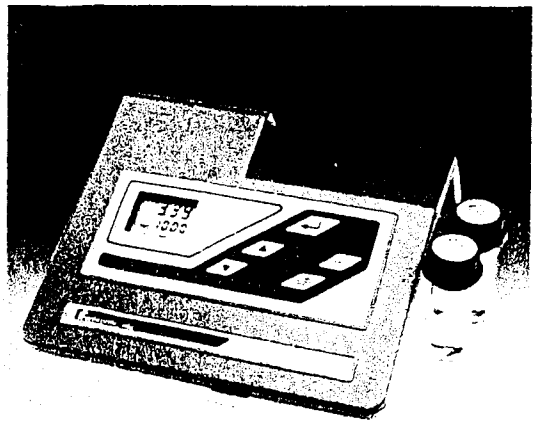
22.2. MICRO 100 Operators Manual, HF scientific, inc., 01/03.

23. TABLES, CHARTS, DIAGRAMS AND VALIDATION DATA

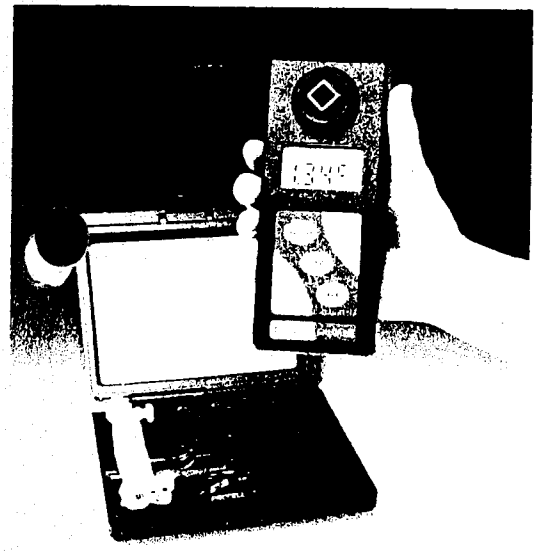
23.1. Micro 100 Operators Manual, HF scientific, inc. 01/03.

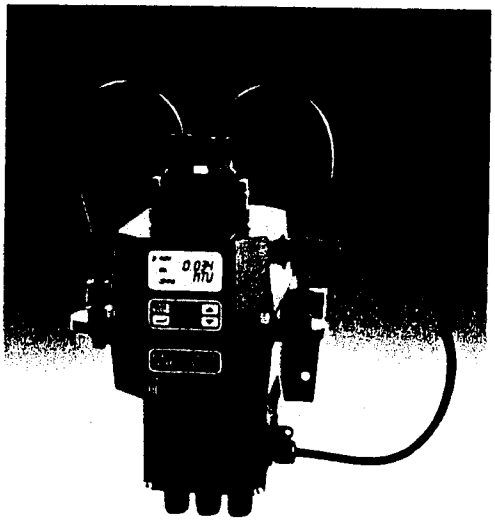
scientific, inc.

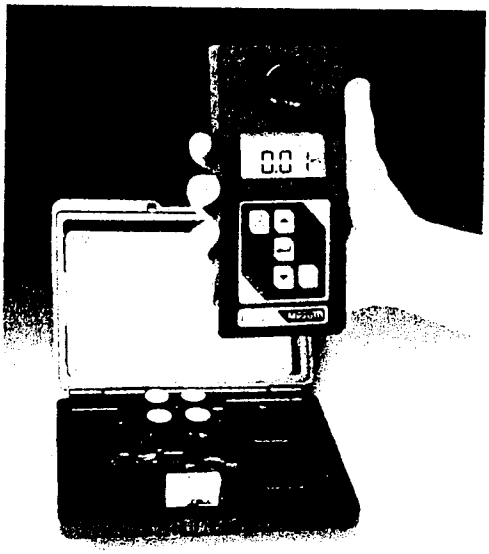


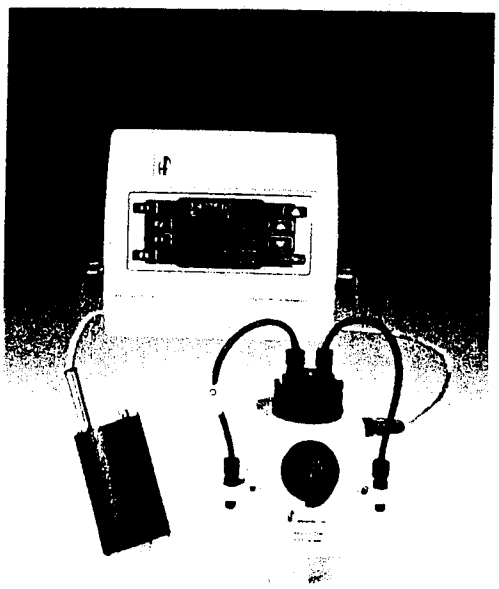


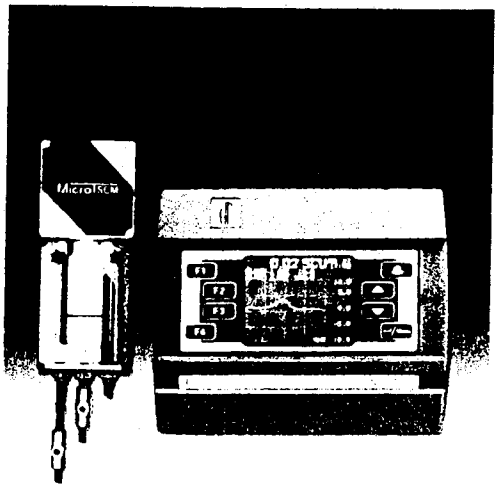
Operators Manual











HF scientific, inc. • 3170 Metro Parkway, Ft Myers, FL 33916 • Phone (239) 337-2116 • Fax (239) 332-7643

DECLARATION OF CONFORMITY

Application of Council Directive: 73/23/EEC

Standard to which Conformity is Declared:

Product Safety	Immunity	EMI
UL3101-1	EN50082-2:1995	EN55011 Group 1 Class A
CSA-C22.2 No. 1010-1-92		Per 50081-2:1994
CE EN61010-1:1993 + A2: 1995		

Meets the requirements of EN61326-1:1997

Manufacture's Name: HF scientific, inc.

Manufacture's Address: 3170 Metro Parkway, Fort Myers, Florida 33916-7597

Importer's Name:

Importer's Address:

Type of Equipment: Turbidimeter

Model No.: Micro 100 Catalog No's 20001/19951
Micro 100IR 19950/19952

I, the undersigned, hereby declare that the equipment specified above conforms to the above Directive and Standard

Place: Fort Myers, Florida USA

Robert J. Maley

(Signature)

Robert J. Maley, President

(Full Name)

TABLE OF CONTENTS

SPECIFICATIONS:

MICRO 100	Conforms to specifications set forth in EPA method 180.1 (Nephelometric Method) §
MICRO 100 IR	Conforms to specifications set forth in ISO 7027: Water Quality - Determination of Turbidity.
Measurement Range	0-1000 NTU
Accuracy†,††	±2% of reading or ±0.01 NTU whichever is greater
Repeatability††	≤ ±1% of reading or ± 0.01 NTU whichever is greater
Resolution	0.01NTU in the range 0.00 – 9.99 NTU 0.1NTU in the range 10.0 – 99.9 NTU 1 NTU in the range 100 – 1000 NTU
Response Time	Less than 6 seconds
Recorder Output	Uni-directional RS232 output
Power Supply	UL, CSA approved 12V DC Wall Mount
Miscellaneous Specifications	1. Year 2000 Compliant 2. Built in Diagnostics 3. Three Year Battery Backup With no External Power
Operating Temperature Range	10°C – 40°C (50°F – 104°F)
Sample Temperature Range	0°C – 50°C (32°F – 122°F)
Dimensions	10.75" W x 10" L x 4.75" H (237mm W x 254mm L x 121mm H)
Shipping Weight	2.5 kg (5.5 lbs.)
Warranty	1 Year from date of shipment

§ The specifications found in EPA method 180.1 are essentially the same as the specifications set out in method 2130B of the Standard Methods for the Examination of Water and Wastewater 19th edition and the specifications set out in ASTM Standard Method D1889-94. The MICRO 100 meets. or exceeds. the specifications set forth in these methods.

† Instrumental accuracy measured under controlled laboratory conditions at 25°C (77°F)

†† Both the accuracy and repeatability specifications for the MICRO 100 are valid only for measurement of static (non-flowing) samples.

1.0 Using This Instruction Manual

Congratulations on your purchase of a new MICRO 100 or MICRO 100 IR Laboratory Turbidimeter (MICRO 100 hereafter). This turbidimeter has been designed for simple and easy measurement of turbidity.

This manual contains simple steps to follow to ensure that your instrument is operating properly. This material assumes that the user knows how to obtain representative samples of their process and has some familiarity with measuring the turbidity of samples[‡] .

The following sections describe how to use and care for your new MICRO 100.

In certain instances NOTES or reminders have been added to give further clarification to the instructions. Refer to the *Table of Contents* or the *Glossary* to easily find specific topics and to learn about unfamiliar terms.

2.0 Unpacking The Instrument

2.1 Packing List of Contents

Item	Qty.
MICRO 100 Laboratory Turbidimeter Instrument	1
Accessory Kit for MICRO 100 (0.02 NTU, 10.0 NTU, 1000 NTU Standards and 2 empty sample cuvettes)	1
MICRO 100 Laboratory Turbidimeter Instruction Manual	1
Power Supply for the MICRO 100	1

2.2 Unpacking and Inspection of the Instrument and Accessories

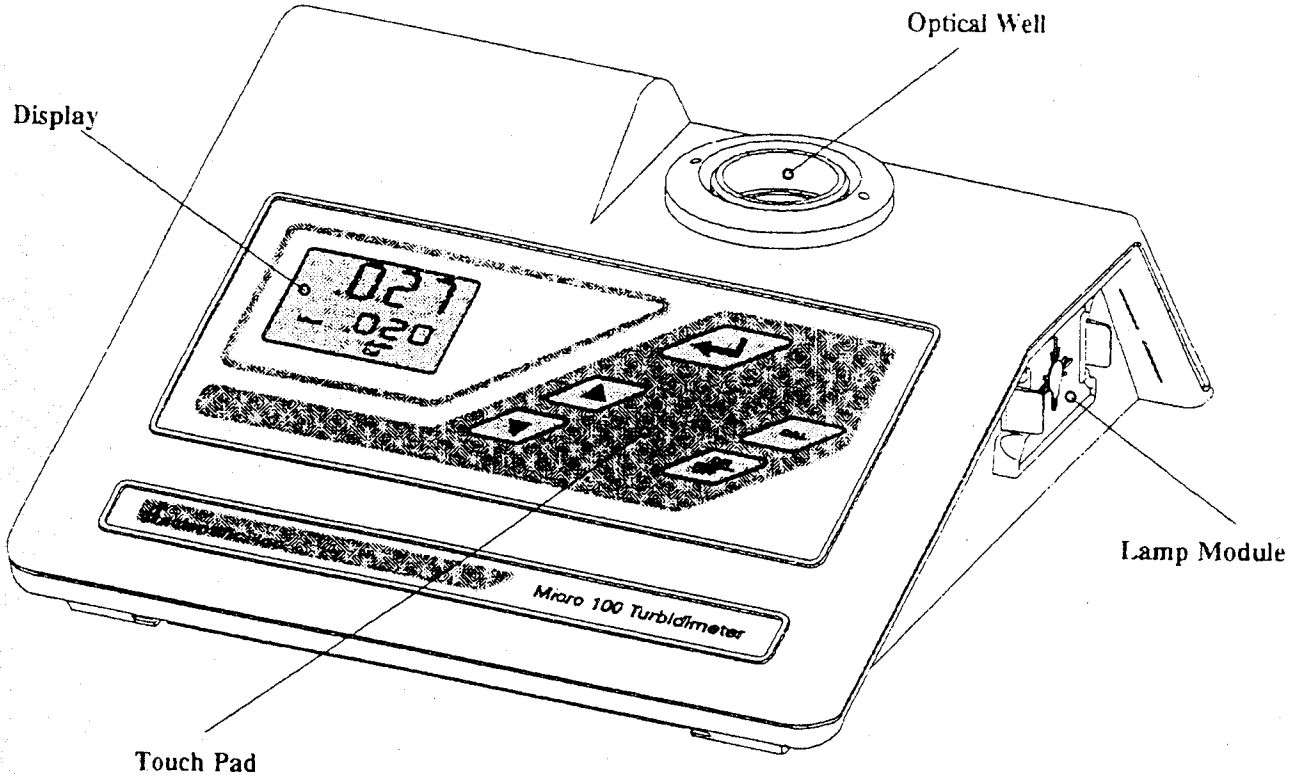
Remove the Accessory Kit (blue case) and the instrument from the packing carton. Carefully inspect all items to ensure that no visible damage has occurred during shipment. If the items you received do not match your order, please immediately contact your local distributor or the HF scientific, inc. Customer Service department.

NOTE: Extra care should be taken when unpacking, opening, and handling the calibration standards and sample cuvettes in the Accessory Kit; surface scratches or finger smudges on the cuvette surface may cause measurement errors. Handle these items by the top area of the cuvette only.

[‡] If you need more information on turbidity please see section 2130 of the 19th edition of the Standard Methods for the Examination of Water and Wastewater.

3.0 Becoming Familiar with The Instrument

Figure 1 is a depiction of the front of the MICRO 100. Not shown in this picture are the RS-232 serial printer port and the 12V DC power plug connector, which are located on the back panel of the instrument.



The user interface of the MICRO 100 has been designed with a 5 key touchpad and user display. The five keys of the Touch Pad and their functionality are described below:

The key is used to turn the instrument on and off. The key is used to enter, or exit, calibration mode. The and are used to set numerical values and to scroll through lists. The key stores value on the screen and/or causes the turbidity data to be output to the printer port when pressed.

Figure 2 illustrates all the items that can appear on the display. The upper row of the display (1) is used for reporting the turbidity levels and to provide user guidance in the customer settings routine. The lower row of the display (2) is used to display the stored turbidity reading and to communicate error messages and user guidance. The display has several status indicators (3) which distinguish the operation of the instrument. In addition, the "**LoBat**" block (4) flashes when the batteries need to be replaced. Finally, several indicators (5) provide guidance when the customer settings routine is being used and when the calibration routine is being used.

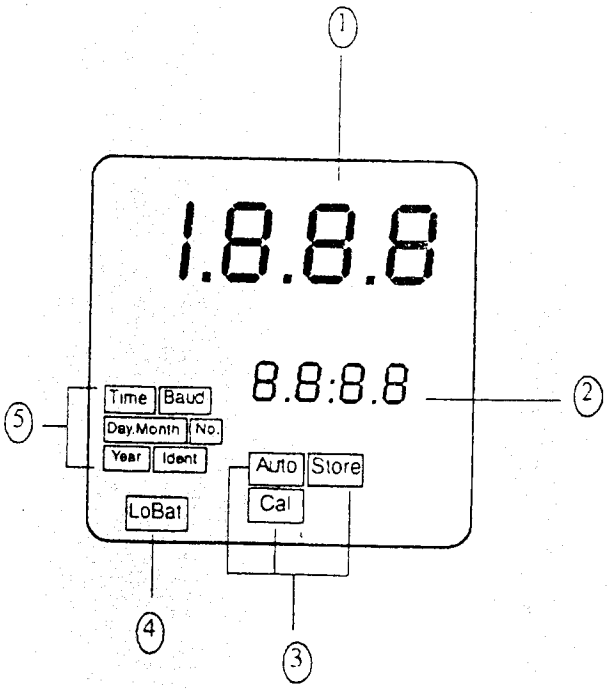


Figure 2

Micro 100 LCD Display

4.0 Routine Operation

The MICRO 100 measures and reports the turbidity of a sample in nephelometric turbidity units (NTU).

NOTE: Nephelometric turbidity units (NTU's) are numerically equivalent to Formazin turbidity units (FTU's) (See Glossary).

Sections 4.1 and 4.2 describe how to use the MICRO 100 under normal operating conditions. These sections include details on how to input certain customer selectable parameters and how to take normal, routine turbidity measurements using the MICRO 100.

4.1 Grab Sample Measurement (Routine Measurement)

The following steps describe how to measure the turbidity of a sample using the MICRO 100:

1. Turn on the MICRO 100. The instrument will be in the normal mode (the "**AUTO**" block should be illuminated). Allow instrument to warm up for at least 30 minutes.
2. Sample approximately 100 ml of the process stream as you would normally do for turbidity measurement.
3. Obtain a clean and dry sample cuvette.
4. Rinse the cuvette with approximately 20 ml of the sample water (2/3 of cuvette volume), capping the cuvette with the black light shield (cuvette top) and inverting several times. Discard the 20 ml of used sample and repeat the rinsing procedure two more times.
5. Completely fill the rinsed cuvette (from step 4) with the remaining portion (approximately 30 ml) of the grab sample and then cap the cuvette with the black light shield. Ensure that the outside of the cuvette is dry, clean and free from smudges**.
6. Place the cuvette in the MICRO 100 and index the cuvette to the lowest reading (the displayed turbidity is continuously updated on the upper row of the display). Once the cuvette is indexed, the reading displayed on the MICRO 100 display should be recorded as the sample turbidity (see Glossary for more information on indexing a cuvette).

** Any typical glass cleaner can be used along with a lint free cloth, or tissue, to clean the outside of the cuvette.

7. If you are measuring and comparing more than one sample, pressing the enter key ↵ will display the latest reading (displayed on the lower row of the display). In addition, if you have selected printer output in the customer setup section pressing the enter key ↵ will output data to the RS232 port.
8. Repeat steps 2 through 7 for all of your samples.

NOTE: The Micro 100 may display - - - for a few seconds while it determines the correct reading.

NOTE: An indication of ⌐| |⌐ (over-range) in the upper row of the display indicates that the standard in the sample well is higher than 1000 NTU.

WARNING: *NEVER* pour liquid directly into the sample well of the MICRO 100, always use a cuvette. The MICRO 100 will accurately measure the turbidity of a sample using only cuvettes with the black light shield on the cuvette (provided by HF scientific, inc.) or the optional pour through assembly.

4.2 Pour Through Sample Measurement (Optional Accessory)

Install the pour through assembly and index it according to the instruction sheet that accompanies the assembly. The following steps describe how to measure the turbidity of a sample using the MICRO 100 fitted with the optional pour through assembly:

1. Turn on the MICRO 100. The instrument will be in the normal automatic mode (the "**AUTO**" block should be illuminated). Allow instrument to warm up for at least 30 minutes.
2. Sample approximately 500 ml of the process stream as you would normally do for turbidity measurement.
3. Pour the complete 500 ml sample into the pour through assembly. Record the turbidity of the sample displayed after the entire 500 ml sample has been poured into the assembly and the flow to drain has ceased, and after the reading has stabilized.
4. If you are measuring and comparing more than one sample, pressing the enter key ↵ will store the reading (displayed on the lower row of the display). In addition, if you have selected printer output in the customer setup section pressing the enter key ↵ will output data to the RS232 port.
5. Repeat steps 2 through 4 for all of your samples.

The sample cuvette used in the pour through assembly is identical to the two standard sample cuvettes supplied with the MICRO 100. Clean the cuvette on a periodic basis according to your experience with the type and turbidity of the sample found in your facility.

5.0 Calibration Procedures

The MICRO 100 Laboratory Turbidimeter has been factory-calibrated using HF scientific, inc. calibration standards that are traceable to the primary turbidity calibration standard, Formazin. It is possible to use the instrument directly out of the box. However, re-calibration of the instrument using the calibration set included is recommended to allow the user to become familiar with the operation of the instrument and the calibration procedures.

HF scientific, inc. recommends that you use the following materials during calibration to achieve the accuracy stated in this manual:

1. De-ionized water filtered through a 0.2 µm filter, or 0.02 NTU Calibration Standard available from HF scientific, inc.
2. 10.0 NTU Formazin primary standard, or 10.0 NTU Calibration Standard available from HF scientific, inc.
3. 1000 NTU Formazin primary standard, or 1000 NTU Calibration Standard available from HF scientific, inc.

Under normal conditions, re-calibration is recommended at least once every three months[††]. You can select a predetermined calibration interval (see section 5.3) for automatic prompting for calibration: if you exceed the selected calibration interval, the "**Cal**" block will flash until the instrument is re-calibrated.

NOTE: **It is well known that diluted Formazin is unstable. If you choose to use Formazin to calibrate the MICRO 100, ensure that you are using a fresh stock suspension of Formazin to achieve the accuracy quoted for the MICRO 100. A Formazin Stock Solution Kit is available from HF scientific, inc. (Catalog No. 50040). The HF scientific, inc. calibration standards (Catalog No.19957 or 19961) are more stable than formazin and have a shelf life of 1 year. If you use the stable HF calibration standards to calibrate the instrument, review the expiration date to ensure that the standards have not expired.**

NOTE: The MICRO 100 must be re-calibrated after lamp replacement.

5.1 Indexing the Calibration Standard(s)

The United States Environmental Protection Agency (US EPA) recommends that cuvettes used for instrument calibration or sample measurement be indexed. To comply with this recommendation, each HF scientific, inc. calibration standard is supplied with an indexing ring and each MICRO 100 is supplied with an indexing pin for quick and repeatable indexing of the calibration standard. The white indexing pin is installed on the collar ring around the optical well.

To index a calibration standard perform the following steps:

1. Slowly rotate the calibration standard one complete revolution (360°).
2. While rotating the standard, observe the Micro 100 and locate the cuvette position with the lowest turbidity reading.
3. With the calibration standard positioned at the location having the lowest turbidity reading, install the Indexing Ring over the black light shield on the standard so that the pointer of the Ring aligns with the Indexing Pin.

5.2 Calibration Procedure

Even though it is possible to calibrate the MICRO 100 using any sequence of the prescribed calibration standards, to achieve the stated accuracy you must use the procedure below to calibrate the instrument.

[††]The MICRO 100 must be re-calibrated with the primary standard (Formazin) at least once every three months if it is to be used for reporting to regulatory agencies

1. Press the key. Once this key is pushed the "**Ident**" block and the "**Cal**" block will illuminate on the display.
2. The turbidity value displayed in the lower row of the display should read 1000 NTU. This is the first standard that must be used in calibration. Insert the 1000 NTU calibration standard into the sample well (see figure 3) by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard) and wait for the reading to stabilize.

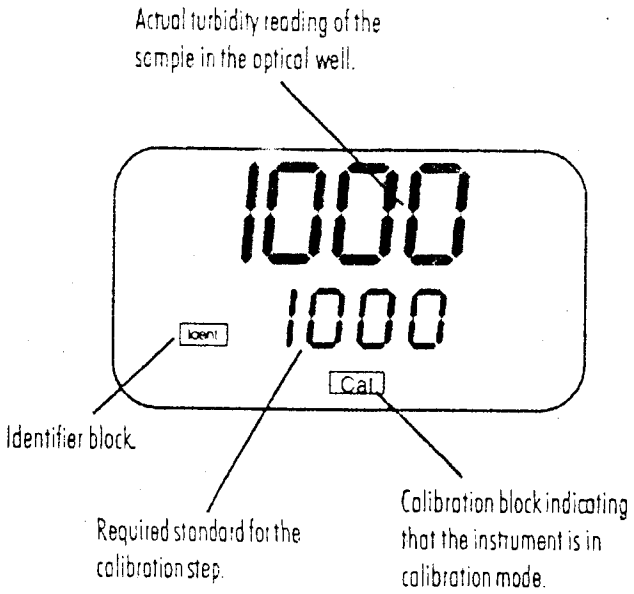


Figure 3
Display appearance during calibration of the 1000 NTU standard

3. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 1000 NTU level (the "**Store**" block will flash) and the upper row of the display should display 1000 NTU. The lower row of the display now shows that the 10.0 NTU calibration standard should be placed in the sample well for continuing the calibration sequence.
4. Insert the indexed 10.0 NTU calibration standard into the sample well by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard) and wait for the reading to stabilize.
5. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 10.0 NTU level (the "**Store**" block will flash) and the upper row of the display should display 10.0 NTU. The lower row of the display now shows that the 0.02 NTU calibration standard should be placed in the sample well for continuing the calibration sequence and wait for the reading to stabilize.
6. Insert the indexed 0.02 NTU calibration standard into the sample well by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard).
7. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 0.02 NTU level. The instrument automatically exits out of the calibration mode and then returns to the normal automatic mode. The display should read 0.02 NTU since this is the turbidity level of the standard that is still in the sample well. At this point, you have calibrated the instrument so that it measures accurately across the full range of the instrument.
8. Proceed to use the instrument normally.

NOTE: During calibration, the MICRO 100 will perform some system self-diagnostics. Several error messages may be displayed. If there is an error, one of the four error messages E01, E02, E03, and E04 will be displayed in the lower row of the display (see section 7.2).

NOTE: At any point in time during calibration, you can cycle through the required calibration points (0.02 NTU, 10 NTU, and 1000 NTU) by pressing either the or keys to individually calibrate with a particular calibration standard. If you wish to exit the calibration mode you may do so at any time by simply pressing the key. However, exiting the calibration process without completing the steps for calibration may cause the accuracy of the instrument to be diminished.

6.0 User Selectable Parameters

The MICRO 100 provides you the ability to customize your instrument according to your needs at any time during normal operation. This section describes how you can customize your instrument.

NOTE: You cannot access any of the user selectable parameters during calibration.

Enter the customer selectable parameters section of the MICRO 100 by simultaneously pressing the ▲ key while holding down the ▼ key when the instrument is operating in the normal automatic mode. The "**Year**" block will be highlighted and the year will be displayed.

NOTE: To skip the selection of any parameter simply press the enter key ↵ to continue on to the next section.

6.1 Setting the Year

With the "**Year**" block highlighted and the year displayed, change the displayed year using the ▲ or ▼ keys. When you have selected the proper year press the enter ↵ key to accept the year.

6.2 Setting the Day and Month

After pressing the ↵ key, the "**Day.Month**" block will be displayed and you will see two numbers on the lower row of the display. The number flashing corresponds to the month. Select the correct month by pressing the ▲ or ▼ key to change the displayed month. When you have selected the proper month, press the ↵ key. After pressing the ↵ key, the "**Day.Month**" block will still be displayed and the second number on the lower row of the display will be flashing: this number corresponds to the day of the month. Select the correct day by pressing the ▲ or ▼ keys to change the displayed day. When you have selected the proper day, press the ↵ key.

NOTE: The MICRO 100 is year 2000 (Y2K) compliant and automatically adjusts for leap years.

6.3 Setting the Time

After pressing the ↵ key, the "**Time**" block will be displayed and you will see the time displayed on the lower row of the display in 24 hour format. The number flashing corresponds to the hour. Select the correct hour by pressing the or key to change the displayed hour. When you have selected the proper hour, press the ↵ key. After pressing the ↵ key, the" **Time**" block will still be displayed and the second number on the lower row of the display will be flashing: this number corresponds to minutes. Select the correct minutes level by pressing the ▲ or ▼ key to change the displayed minutes. When you have selected the proper minutes level, press the ↵ key.

6.4 *Setting the Calibration Interval*

After pressing the ↵ key, the upper row of the display will have the letters **"Int"** printed in it. This corresponds to the calibration time interval. The number in the lower row of the display corresponds to the number of days that you wish to have between scheduled calibrations (default is 30 days). Select the desired number of days between scheduled calibrations by pressing the ▲ or ▼ key to change the displayed day. In normal automatic mode, if you exceed this number of days between calibration, the **"Cal"** block will flash until you re-calibrate the instrument. When you have selected the desired calibration interval press the ↵ key.

6.5 *Setting the Printing Function*

After pressing the ↵ key, the upper row of the display will have the letters **"Prt"** printed in it. This feature allows you to turn the printing option on the instrument on or off. Select the desired printing action (on or off) by pressing the ▲ or ▼ key. When you have selected the proper printing option press the ↵ key.

If you selected to turn off the printing function, pressing the ↵ key will return you back to the normal mode of the instrument. If, on the other hand, you chose to turn on the printing function, pressing the ↵ key will cause the **"Baud"** block to be highlighted and you can select the correct baud rate for operation of your printer. Select the desired baud rate (1200, 2400, 4800, or 9600) by pressing the ▲ or ▼ key to change the displayed baud rate. The other RS 232 parameters are fixed at 2 stop bits, 8 data bits and odd parity. Once you have selected the proper baud rate press the ↵ key. Pressing the ↵ key will return you back to the normal automatic mode of the instrument.

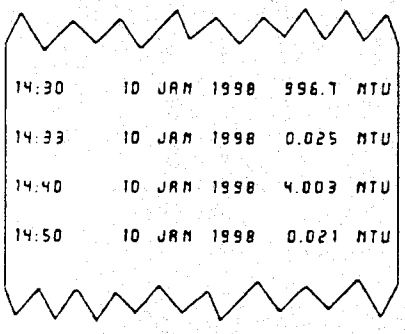


Figure 4

By turning on the printing function, you have instructed the instrument to print out specific information. When the ↵ key is pressed during the normal mode, information is output on the sample in the optical well (See Figure 4). This figure shows the information printed for four different samples. The format of the information is time, date and turbidity level.

Also, a specific message will be printed out upon exit or completion of the calibration routine (See Figure 5). This printout shows all of the information that is pertinent to the calibration status of the instrument.

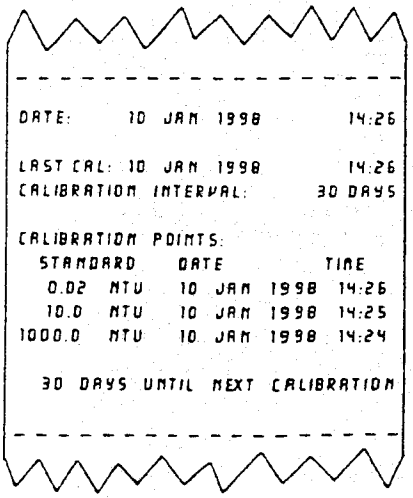


Figure 5

6.6 *Completing Selectable Parameters*

You have now completed the customer selectable parameters section of the instrument. You can enter this menu at any time to re-set, or change any of the parameters.

7.0 Troubleshooting

7.1 System Warning Message(s)

Automatic warning messages are generated by the MICRO 100 to provide you with specific diagnostic information about the instrument. These messages are for your use and do not reduce the performance of the instrument.

7.1.1 Flashing "Cal" block

A flashing **"Cal"** block observed during normal automatic mode indicates that you should recalibrate your instrument. The factory default is 30 days. HF recommends calibration every 30 days. The flashing **"Cal"** block is only a warning and does not mean that the instrument will stop performing accurately. The **"Cal"** block will flash until you have recalibrated the instrument.

7.1.2 Flashing "LoBat" block

A flashing **"LoBat"** block on the display indicates that the backup batteries need to be replaced. Under this condition, the parameters that are stored in memory (all of the user settable parameters and the instrument calibration) may be lost under conditions when power is not supplied to the instrument. See section 8.3 for instructions on replacing the batteries.

7.2 System Error Message(s)

Error messages are generated by the MICRO 100 when it detects problems with the instrument operation. When these messages are observed and if you do not understand the instructions shown below, contact the HF scientific, inc. Technical Services department to determine a resolution to the problem. An error message is indicated by the instrument when an "E-0X" is displayed on the lower row of the display. The MICRO 100 has five error codes, each assessing a different component or system of components in the instrument. The following table lists the error messages and their associated meanings.

ERROR MESSAGE	ASSOCIATED MEANING	TYPICAL CAUSE
E-01	Overall light level detected is too low during calibration	Wrong standard is in the optical well or lamp failure
E-02	Overall light level detected is too high during calibration	Wrong standard is in the optical well.
E-03	Amount of light detected between 0.02 NTU and 10.0 NTU is too small during calibration	Wrong standard is in the optical well or bad A/D circuitry
E-04	Amount of light detected between10.0 NTU and 1000 NTU is too small during calibration	Wrong standard is in the optical well or bad A/D circuitry
E-05	Amount of light detected is too low during normal mode	Lamp failure

If errors 1-4 are noted, turn the instrument off and then back on. Once the instrument is back on, re-calibrate the instrument. If the error persists, please contact the HF scientific, inc. Technical Services Department to rectify the error. (See Section 9.0)

If error 5 is noted, replace the lamp module with a spare lamp module. If you do not have a spare lamp module, refer to Section 10.0 for ordering information.

7.3 Factory Default Parameters

The MICRO 100 memory retains all original factory settings. At any time, you can force the instrument to change back to these default settings. All calibration values and settable parameters (see section 5 & 6) will change back to their original configurations. This is particularly useful if you feel that your calibration standards may have been compromised. In this situation you may use the factory default parameters while waiting for new standards to arrive from HF scientific, inc.

To invoke this option, first turn on the instrument. Next, press the ⌯ key while holding down the ▲ key. The instrument will continue operating in normal automatic mode with all adjustable parameters reset to factory default conditions.

8.0 Routine Maintenance

The MICRO 100 has been designed for ease of use and simple operation. When not in use, ensure that the instrument has been turned off and that a clean sample cuvette fitted with a black light shield cap has been placed in the sample well. This will ensure that a minimal amount of dust and/or debris will be able to settle on the optics of the instrument.

8.1 Cuvette Cleaning and Care

Proper measurement of the turbidity of a sample requires the use of a cuvette that is free of marks, smudges, scratches and any bacterial growth. Cleaning the cuvette is accomplished by washing the interior and exterior of the cuvette in a detergent solution. Once cleaned, the cuvette should be rinsed thoroughly 8 to 10 times with clean distilled water to eliminate the possibility of detergent build-up and streaking. Cleaned and dried cuvettes should be stored with the black light shield cap on the cuvette and can be stored in a cuvette rack (see accessories and replacement parts list). During normal operation you may use any typical glass cleaner along with a lint free cloth, or tissue, to clean the outside of the cuvettes. HF scientific, inc. sells a Cuvette Maintenance Kit Catalog No. 19959 for this purpose.

8.2 Lamp Replacement

Periodically the lamp module will require replacement. Figure 1 illustrates the location of the lamp module. An error message will be illuminated when it is time to replace the lamp (see section 7.2). It is recommended that one spare lamp for each MICRO 100 turbidimeter be kept on hand at all times to ensure continuous use of the instrument.

Before replacing the lamp module ensure that the instrument is turned off. Once you have turned off the instrument, proceed with the following instructions:

Lamp Replacement cont'd.

1. Remove the lamp module from the instrument by squeezing the two side tabs on the module inward while pulling the module out of the instrument. Pull the module away from the instrument until the in-line power connector is exposed (about 6-8 inches).
2. Unfasten the connector by holding on to the white in-line connector and pulling the in-line connector apart. When pulling the in-line connector apart, DO NOT hold on to the wires.
3. The new lamp module can now be connected to the instrument using the in-line power connector.
4. Feed the wire back into the instrument being careful that the wire does not get in the way of the lamp or the lamp holder Z (on instrument). Make sure that the light bulb icon on the back of the lamp module is upright. Press the module into the instrument until you hear it click firmly into place.

Note: The side tabs may need to be pressed outward until they click to secure the new lamp module.

5. If the two side tabs on the lamp module do not click the lamp module securely in place, check that the power wire is not obstructing the lamp module.
6. Turn on the instrument and follow the instructions in section 4.1 to re-calibrate the instrument with the new lamp module. **The instrument must be re-calibrated after lamp module replacement.**
7. Resume normal operation.

8.3 Battery Replacement

The backup of calibration and user preferences requires power. For this reason, the MICRO 100 should be plugged in (it can be left off) when not in use. If the unit is unplugged from the wall receptacle or the provided power supply, the batteries in the MICRO 100 will provide the backup power. As these batteries are non rechargeable and have a finite life, they will need replacement if the instrument is left unplugged for long periods of time.

It is recommended that the battery replacement be performed at HF scientific inc. Please refer to the following section for contact information.

9.0 *Contacting the HF scientific, inc. Technical Service Department*

For technical assistance or to order replacement parts please contact the HF Technical Services Department or Customer Service Department.

HF scientific, inc.
3170 Metro Parkway
Fort Myers, Florida 33916-7597
Phone: (239) 337-2116
Fax: (239) 332-7643
Email: info@hfscientific.com

10.0 Accessories and Replacement Parts List

Accessory or Replacement Part	*Catalog Number*
Micro 100 Calibration Set (includes 0.02 NTU, 10.0 NTU, 1000 NTU Calibration Standards)	19957
Micro 100 IR Calibration Set (includes 0.02 NTU, 10.0 NTU, 1000 NTU Calibration Standards)	19961
Formazin Stock Solution Kit Formazin, 4000 NTU Stock Solution, 500 ml	50040 70914
Lamp Module – Tungsten Filament	19972
Turbidity Free Water	70908
Pour Through Assembly	19975
Cuvette Stand (holds 11 cuvettes)	19981
Sample Cuvettes – 3 pack	50051
Sample Cuvettes – 10 pack	50052
Batteries (set of 2)	70007
RS232 Cable for Serial Printer	19798

Glossary

Formazin Turbidity Units (FTU): *see Nephelometric Turbidity Units*

Indexing a Cuvette: The United States Environmental Protection Agency (US EPA) recommends that cuvettes used for turbidimeter calibration or sample measurement be indexed. To index a cuvette with a sample in it, slowly rotate the cuvette throughout one complete revolution (360°). While rotating the sample cuvette, observe the display and locate the position that the cuvette is in which provides the lowest turbidity reading. This position is the indexed position of the cuvette.

Nephelometric Turbidity Units (NTU): Unit of measure used when comparing the light scattered by a liquid media to the light scattered by a known concentration of Formazin Polymer. This unit of measure is recognized as a measure of the optical clarity of an aqueous sample. NTU is the accepted unit of measurement for turbidity.

Turbidity: 1) A measure of the attenuation of a radiant flux as it passes through a liquid media. 2) Optical clarity of a liquid, 3) a phenomena caused by the presence of undissolved matter in a liquid media.

WARRANTY

HF scientific, inc., as vendor, warrants to the original purchaser of the instruments to be free of defects in material and workmanship, in normal use and service, for a period of one year from date of delivery to the original purchaser. HF scientific, inc.'s, obligation under this warranty is limited to replacing, at its factory, the instrument or any part thereof. Parts which by their nature are normally required to be replaced periodically, consistent with normal maintenance, specifically lamps including fluorescent backlight, reagent, desiccant, sensors, electrodes and fuses are excluded. Also excluded are accessories and supply type items.

Original purchaser is responsible for return of the instruments, or parts thereof, to HF scientific, inc.'s factory. This includes all freight charges incurred in shipping to and from HF scientific, inc.'s factory.

HF scientific, inc. is not responsible for damage to the instrument, or parts thereof, resulting from misuse, negligence or accident, or defects resulting from repairs, alterations or installation made by any person or company not authorized by HF scientific, inc.

HF scientific, inc. assumes no liability for consequential damage of any kind, and the original purchaser, by placement of any order for the instrument, or parts thereof, shall be deemed liable for any and all damages incurred by the use or misuse of the instruments, or parts thereof, by the purchaser, its employees, or others, following receipt thereof.

Carefully inspect this product for shipping damage, if damaged, immediately notify the shipping company and arrange an on-site inspection. HF scientific, inc. cannot be responsible for damage in shipment and cannot assist with claims without an on-site inspection of the damage.

This warranty is given expressly and in lieu of all other warranties, expressed or implied. Purchaser agrees that there is no warranty on merchantability and that there are no other warranties, expressed or implied. No agent is authorized to assume for HF scientific, inc. any liability except as above set forth.

HF scientific, inc.
3170 Metro Parkway
Fort Myers, Florida 33916-7597
Phone: (239) 337-2116
Fax: (239) 332-7643

Title : **SM 2320 B / EPA METHOD 310.1, ALKALINITY (TITRATION METHOD)**

Document No. : SOP-M738
Revision No. : 1.6
Supersedes : 1.5

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PROPRIETARY INFORMATION STATEMENT

Revision 1.6 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/31/15
MANAGEMENT **DATE**

_____ 03.31.15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature
	04/29/16		

1. METHOD IDENTIFICATION

1.1. SM 2320 B / EPA Method 310.1, Alkalinity (Titration Method).

2. APPLICABLE MATRICES

2.1. This method is applicable to natural waters and wastewaters. It is also applicable to soil and solid wastes as a modified method.

2.1.1. The soil and solid waste samples are processed according to the procedure outlined in Section 14.4. The modified method is reported as SM 2320 B(M) or EPA Method 310.1(M).

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

Alkalinity (as $CaCO_3$) Concentration (mg/L or mg/kg)	Aqueous RL (mg/L)	Solid RL (mg/kg)
C < 100	1.0	5.0
100 ≤ C < 1000	5.0	5.0
1000 ≤ C < 10000	10.0	10.0
10000 ≤ C < 100000	100	100
C ≥ 100000	1000	1000

Note: $C = C_T$, C_B, C_C, or C_H

C_T = Total Alkalinity as ($CaCO_3$)

C_B = Bicarbonate Alkalinity as ($CaCO_3$)

C_C = Carbonate Alkalinity as ($CaCO_3$)

C_H = Hydroxide Alkalinity as ($CaCO_3$)

3.2. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used.

4.1.1. Alkalinity is a measure of an aggregate property of water, and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

4.2. Alkalinity of many surface waters is primarily a function of bicarbonate, carbonate, and hydroxide content; hence, it is taken as an indication of the concentration of these constituents.

4.2.1. The measured values may include contributions from borates, phosphates, silicates, or other bases if these are present.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of the instruments and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

4.3.1. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. SM 2320 B / EPA Method 310.1 is used to determine alkalinity from the volume of standard acid required to titrate a portion of sample to a designated pH.

5.1.1. Titration is conducted at ambient (room) temperature with a properly calibrated pH meter.

5.1.2. Sample must not be filtered, diluted, concentrated, or altered.

5.2. For samples of low alkalinity (less than 20 mg/L $CaCO_3$), the amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Since this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero

baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.

6.10. Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.15. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.22. Terms Specific to Alkalinity as Calcium Carbonate Determination

6.22.1. Total Alkalinity: The alkalinity measured by potentiometric titration to pH 4.5 or other appropriate end point.

6.22.2. Phenolphthalein Alkalinity: The alkalinity measured by potentiometric titration to pH 8.3.

6.23. Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.

7. INTERFERENCES

7.1. Improper care of the electrode may cause the pH meter to produce unreliable or erroneous pH readings. Follow the manufacturer's instructions for proper electrode care.

7.2. Sluggish response or unstable reading occurs if the electrode is coated with soaps, oily matter, suspended solids, or precipitates. Clean the electrode as follows:

7.2.1. Place the sensing part of the electrode in warm (60–80°C) reagent water for a few minutes, rinse with clean reagent water, and rehydrate (soak) in pH 7.00 buffer. If pH 7.00 buffer is unavailable, use pH 4.00 buffer instead.

7.3. Touching or moving the electrode cable during pH measurement may cause high impedance (resistance) of the pH glass membrane and result in unstable reading.

7.4. Temperature errors associated with the electrode may be eliminated by using automatic temperature compensation (ATC) probe.

7.4.1. If automatic temperature compensation (ATC) probe is not provided, titrate at 25 ± 5°C.

7.5. Contamination by carryover can occur after each sample is analyzed. To reduce carryover, the electrode should be rinsed with reagent water or a portion of the next solution to be measured, and blot dry (do not wipe) with a tissue wiper between each measurement.

7.6. Salts of weak organic and inorganic acids present in large amounts may cause interferences in the electrometric pH measurements.

8. SAFETY

8.1. Sulfuric acid is corrosive. Hence, precautions must be taken to avoid inhalation, ingestion, or skin contact.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) or Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS or SDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. pH meter, capable of reading to 0.05 pH unit, equipped with ATC probe input and BNC electrode input connectors, Fisher Scientific accumet® Basic pH Meter, Fisher Scientific accumet® Basic AB 15 Bench-Top pH Meter, or equivalent.

9.1.1. Electrode, 0–14 pH range, glass pH membrane sensor, single porous ceramic junction, Ag/AgCl internal reference, rugged standard-size epoxy body, equipped with ATC probe, Fisher Scientific accumet® Liquid-Filled pH/ATC Epoxy Body Combination Electrode or equivalent.

9.1.2. Electrode holder, adjustable height.

9.2. pH Meter Software

9.2.1. None.

9.3. pH Meter Maintenance and Troubleshooting

9.3.1. Refer to the pH meter user manual for pH meter maintenance and troubleshooting.

9.4. Specimen containers, 4.5 oz (120 mL), high density polyethylene (HDPE) or polypropylene, with polypropylene lids, disposable.

9.5. Beakers, 250 mL or other capacity, glass, Class A.

9.6. Volumetric flasks, 500 mL or other capacity, glass, Class A.

9.7. Graduated cylinders, 50 mL or other capacity, glass, Class A.

9.8. Titration apparatus:

9.8.1. Reservoir bottles, 1 L and 2 L, clear glass.

9.8.2. Burets, 10.00 mL (0.05 mL subdivision), 25.0 mL (0.1 mL subdivision), and 50.0 mL (0.1 mL subdivision), borosilicate glass, with PTFE stopcock, Class A.

9.8.3. Aspirator bulbs, rubber.

9.9. Ultrasonic bath, VWR Scientific Aquasonic Model 550T or equivalent.

9.10. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.11. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.12. Spatula, stainless steel.

9.13. Magnetic stirrer.

9.14. Stir bar, Teflon coated.

9.15. Stir bar retriever, magnetic.

9.16. Tissue wipers, 1-ply, antistatic, KIMTECH Science Kimwipes® Delicate Task Wipers, KIMTECH Science Kimwipes® Precision Wipes Tissue Wipers, or equivalent.

9.17. Wash bottle, 1 L.

9.18. Drying oven, capable of maintaining 250 ± 10°C.

9.19. Desiccator.

9.20. Watch glass.

9.21. Hot plate.

9.22. Thermometer.

9.23. Forceps or tongs, stainless steel.

9.24. Gloves, heat resistant.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, carbon dioxide free, distilled or deionized.

10.1.1.1. Boil reagent water for 15 minutes and cool to ambient temperature prior to standard preparation.

10.1.1.2. The final pH of the reagent water should be ≥ 6.00, and the conductivity should be < 2 µmho/cm.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium carbonate, Na_2CO_3, anhydrous, 105.99 molecular weight (or 53.00 equivalent weight), white powder, certified, reagent grade or equivalent.

10.1.3.1. Dry 53–55 g of sodium carbonate by baking at 250°C for 4 hours on a watch glass, and cool in a desiccator.

10.1.4. Calcium carbonate, $CaCO_3$, 100.09 molecular weight (or 50.04 equivalent weight), white powder, certified, reagent grade or equivalent.

10.1.5. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified and NIST traceable stock standard solution, in sealed polypropylene bottle, containing 0.02 N (N/50) of sulfuric acid in reagent water (1.00 mL = 1.00 mg $CaCO_3$), is used to determine alkalinity as calcium carbonate.

10.2.2. Pre-certified and NIST traceable stock standard solution, in sealed polypropylene bottle, containing 0.1 N (N/10) of sulfuric acid in reagent water (1.00 mL = 5.00 mg $CaCO_3$), is used to determine alkalinity as calcium carbonate.

10.2.3. Manually-prepared stock standard solution, in a sealed volumetric flask, containing sodium carbonate in reagent water (1.00 mL = 50 mg $CaCO_3$), is used to prepare spike standard.

10.2.3.1. Prepare the Na_2CO_3 solution by dissolving 52.9473 ± 0.0001 g of Na_2CO_3 in carbon dioxide free reagent water and dilute to 1000 mL with additional carbon dioxide free reagent water.

10.2.3.1.1. Due to extremely low solubility of $CaCO_3$ in water, Na_2CO_3 is used in place of $CaCO_3$ for spike standard preparation.

10.2.3.2. The stock standard solution must be stored under dark and refrigerated conditions, and replaced after six months or sooner if routine QC indicates a problem.

10.2.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250 mL pre-cleaned high density polyethylene (HDPE) or clear glass containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.2. Solid samples should be collected in 4 oz pre-cleaned clear glass wide-mouth jars or 6 in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Samples shall be maintained in a chilled state, 0–6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions.

11.3.1. Samples must be analyzed within 14 days of sample collection.

11.3.2. Sample should be protected from agitation and prolonged exposure to air prior to analysis.

11.3.3. Waste samples may be subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air. If biological activity is suspected, analyze the samples as soon as feasible, preferably within 24 hours of sample collection.

11.4. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. Event Based Quality Control (MBs and LCS/LCSDs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS), and a laboratory control sample duplicate (LCSD).

12.1.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.1.3. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively, and the RPD (between LCS/LCSD) is ≤ 20%.

12.1.4. The acceptance criteria for MBs are as follows:

12.1.4.1. The concentrations of target analytes in an MB should be ≤ ½ the respective reporting limits (RLs). If the concentration of any target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated.

12.1.4.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.1.4.3. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

12.2. Matrix Based Quality Control (Sample Duplicates)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a sample duplicate.

12.2.1.1. A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples.

12.2.2. The acceptance criteria for duplicate compounds are as follows:

12.2.2.1. The RPD is ≤ 25%.

12.2.2.2. When the RPD of the duplicate compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. If the RPD of the duplicate compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.2.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.3. If the %REC or RPD of the LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.4. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Top Loading Balance

13.2.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.2.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.3. Thermometer

13.3.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

13.4. pH Meter and Electrode

13.4.1. Calibrate the pH meter and electrode with fresh pH 4.00, pH 7.00, and pH 10.00 buffers as described in Appendix A daily prior to sample analysis and after every batch of 20 samples or portion thereof within a 24-hour shift.

13.5. Sulfuric Acid Titrant Standardization

13.5.1. Standardize each H_2SO_4 stock standard solution against 0.05-N Na_2CO_3 stock standard solution as described in Appendix B.

14. PROCEDURE

14.1. pH Meter and Electrode Setup

14.1.1. Verify that the fill hole of the electrode is in the open position.

14.1.1.1. If the fill hole is in the closed position, rotate the blue cap ring clockwise until the fill hole is in the open position.

14.1.2. Verify that the electrolyte level in the reference cavity (outer annular space) of the electrode is sufficiently high.

14.1.2.1. If the electrolyte level is lower than ¼ inch below the cap, add electrode refilling solution.

14.1.3. Verify that the electrode and the ATC probe are connected to the pH meter securely.

14.1.3.1. The pH meter will adjust for varying temperature continuously when the ATC probe is connected.

14.1.3.2. The default temperature of the pH meter is set at 25°C if the ATC probe is not connected.

14.1.4. Verify that the meter screen is in pH mode.

14.1.4.1. For accumet® Basic pH Meter, press and release the "pH/mV" button to toggle between pH, mV, and relative mV (rel mV) modes.

14.1.4.2. For accumet® Basic AB 15 Bench-Top pH Meter, press and release the "mode" button to toggle between pH, mV, and relative mV (REL mV) modes.

14.2. Aqueous Sample Preparation

14.2.1. Measure the ambient temperature with a calibrated thermometer. Record the temperature to the nearest 0.1°C.

14.2.2. Allow an aqueous sample to reach ambient temperature.

14.2.3. Measure 50 ± 1 mL of the aqueous sample into a clean specimen container containing a stir bar. Record the volume to the nearest 1 mL.

14.2.3.1. For MB/LCS/LCSD, measure exactly 50 mL of clean reagent water.

14.2.4. Add 100 µL of the spike stock standard solution to all laboratory control samples.

14.2.5. Proceed to Section 14.5. for potentiometric titration.

14.3. Aqueous Sample Preparation for Low Alkalinity (< 20 ppm) Determination

14.3.1. Measure the ambient temperature with a calibrated thermometer. Record the temperature to the nearest 0.1°C.

14.3.2. Allow an aqueous sample to reach ambient temperature.

14.3.3. Measure 100 ± 1 mL of the aqueous sample into a clean specimen container containing a stir bar. Record the volume to the nearest 1 mL.

14.3.3.1. For MB/LCS/LCSD, measure exactly 100 mL of clean reagent water.

14.3.4. Add 20 µL of the spike stock standard solution to all laboratory control samples.

14.3.5. Proceed to Section 14.6. for potentiometric titration of low alkalinity.

14.4. Solid Sample Preparation

14.4.1. Measure the ambient temperature with a calibrated thermometer. Record the temperature to the nearest 0.1°C.

14.4.2. Homogenize a solid sample as outlined in the current revision of SOP-M230.

14.4.3. Measure 20.0 ± 0.5 g of the homogenized solid sample into a clean specimen container. Record the mass to the nearest 0.1 g.

14.4.3.1. For MB/LCS/LCSD, measure exactly 20.0 g of washed sea sand. Record the washed sea sand identification number.

14.4.4. Add 40 µL of the spike stock standard solution to all laboratory control samples.

14.4.5. Add exactly 100 mL of reagent water to the specimen container.

14.4.6. Cap the specimen container and shake to mix the solid sample.

14.4.7. Place the specimen container in the ultrasonic bath and sonicate the solid sample for 30 minutes.

14.4.8. Allow the solid phase to settle.

14.4.9. Measure 50 ± 1 mL of the supernatant into a clean specimen container containing a stir bar.

14.4.10. Proceed to Section 14.5. for potentiometric titration.

14.5. Potentiometric Titration

14.5.1. Assemble a titration apparatus with a 25.0 mL or 50.0 mL buret, the calibrated pH meter and electrode, and a magnetic stirrer.

14.5.1.1. Use the 50.0 mL buret for the 0.02-N sulfuric acid titrant.

14.5.1.2. Use the 25.0 mL or 50.0-mL buret for the 0.1-N sulfuric acid titrant.

14.5.2. Initialize the buret to 0.0 mL by squeezing the aspirator bulb to dispense the sulfuric acid titrant into the buret.

14.5.2.1. If the sample alkalinity is suspected to be < 1000 ppm, use the 0.02-N sulfuric acid titrant for the titration procedure.

14.5.2.2. If the sample alkalinity is suspected to be ≥ 1000 ppm, use the 0.1-N sulfuric acid titrant for the titration procedure.

14.5.3. Measure the initial pH of the sample with the magnetic stirrer operating. Stir the sample gently throughout the titration procedure. Record the initial pH to the nearest 0.01 pH unit.

14.5.4. If the initial pH is > 8.3, proceed to Section 14.5.5. If the initial pH is ≤ 8.3, proceed to Section 14.5.8.

14.5.5. Slowly add the sulfuric acid titrant to the sample and titrate to pH 8.3. As the end point is approached, make smaller additions of the sulfuric acid titrant, and allow the pH equilibrium to be reached before adding more titrant.

14.5.6. When the reading is stable, record the volume of the sulfuric acid titrant used to the nearest 0.1 mL. The volume of the titrant used to reach pH 8.3 is applied for the calculation of phenolphthalein alkalinity.

14.5.6.1. For accumet® Basic pH Meter, the meter screen displays the "S" icon when the reading is stable.

14.5.6.2. For accumet® Basic AB 15 Bench-Top pH Meter, the meter screen displays the "STABLE" icon when the reading is stable.

14.5.7. Continue the titration without initializing the buret and without undue delay.

14.5.8. Slowly add the sulfuric acid titrant to the sample and titrate to pH 4.5. As the end point is approached, make smaller additions of the sulfuric acid titrant, and allow the pH equilibrium to be reached before adding more titrant.

14.5.8.1. If the volume of the 0.02-N sulfuric acid titrant required to reach pH 4.5 is ≥ 50 mL, re-prepare the sample and use the 0.1-N sulfuric acid titrant for the titration procedure.

14.5.8.2. If the 0.1-N sulfuric acid titrant in the 25.0 mL buret is used for titration, and the volume of the 0.1-N sulfuric acid titrant required to reach pH 4.5 is ≥ 25 mL, re-prepare the sample and use the

0.1-N sulfuric acid titrant in the 50.0 mL buret for the titration procedure.

14.5.8.3. If the 0.1-N sulfuric acid titrant in the 50.0 mL buret is used for titration, and the volume of the 0.1-N sulfuric acid titrant required to reach pH 4.5 is ≥ 50 mL, re-prepare the sample with reduced sample size and use the 0.02-N or 0.1-N sulfuric acid titrant for the titration procedure.

14.5.8.4. Measuring an un-buffered solution, such as MB, may require more time for the electrode to stabilize. It may take several minutes, and the response may appear adrift.

14.5.9. When the reading is stable, record the total volume of the sulfuric acid titrant used to the nearest 0.1 mL and the final pH to the nearest 0.01 pH unit. The total volume of the titrant used to reach the final pH is applied for the calculation of total alkalinity.

14.5.9.1. For accumet® Basic pH Meter, the meter screen displays the "S" icon when the reading is stable.

14.5.9.2. For accumet® Basic AB 15 Bench-Top pH Meter, the meter screen displays the "STABLE" icon when the reading is stable.

14.5.10. If the total alkalinity of an aqueous sample from calculation is < 20 ppm, re-prepare the aqueous sample for low alkalinity determination, and proceed to Section 14.6.

14.6. Potentiometric Titration of Low Alkalinity (< 20 ppm)

14.6.1. Assemble a titration apparatus with a 10.00 mL buret, the calibrated pH meter and electrode, and a magnetic stirrer.

14.6.1.1. Use the 10.00 mL buret for the 0.02-N sulfuric acid titrant.

14.6.2. Initialize the buret to 0.00 mL by squeezing the aspirator bulb to dispense the sulfuric acid titrant into the buret.

14.6.3. Measure the initial pH of the sample with the magnetic stirrer operating. Stir the sample gently throughout the titration procedure. Record the initial pH to the nearest 0.01 pH unit.

14.6.4. Slowly add the sulfuric acid titrant to the sample and titrate to pH 4.3–4.7. As the pH range is approached, make smaller additions of the sulfuric acid titrant, and allow the pH equilibrium to be reached before adding more titrant.

14.6.4.1. Measuring an un-buffered solution, such as MB, may require more time for the electrode to stabilize. It may take several minutes, and the response may appear adrift.

14.6.5. When the reading is stable, record the volume of the sulfuric acid titrant used to the nearest 0.1 mL and the intermediate pH to the nearest 0.01 pH unit. The volume of the titrant used to reach the intermediate pH is applied for the calculation of total alkalinity.

14.6.5.1. For accumet® Basic pH Meter, the meter screen displays the "S" icon when the reading is stable.

14.6.5.2. For accumet® Basic AB 15 Bench-Top pH Meter, the meter screen displays the "STABLE" icon when the reading is stable.

14.6.6. Continue the titration without initializing the buret.

14.6.7. Carefully add the sulfuric acid titrant to the sample and reduce the pH exactly 0.30 pH unit. As the end point is approached, make smaller additions of the sulfuric acid titrant, and allow the pH equilibrium to be reached before adding more titrant.

14.6.8. When the reading is stable, record the total volume of the sulfuric acid titrant used to the nearest 0.1 mL and the final pH to the nearest 0.01 pH unit. The total volume of the titrant used to reach the final pH is applied for the calculation of total alkalinity.

14.7. Samples are analyzed one at a time in the following or other logical order:

1) Method Blank (MB)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Samples (up to 20 per batch, excluding MBs and QC check samples)
5) Sample Duplicate

14.7.1. Item 1: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.7.1.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.

14.7.1.2. One MB is required every day preparatory methods (i.e., sonications, titrations, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.2. Item 2: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.7.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.7.2.2. One LCS is required every day preparatory methods (i.e., sonications, titrations, etc.) are performed for every batch of 20

samples per matrix or portion thereof, whichever is more frequent.

14.7.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.2.

14.7.4. Item 4: Up to 20 samples (excluding method blanks and QC check samples) per batch.

14.7.5. Item 5: The sample duplicate is a selected field sample re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.

14.7.5.1. The purpose of the sample duplicate is to assess matrix effects. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.2.

14.7.5.2. One sample duplicate is required daily for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.8. Thoroughly document all aspects of the sample preparation and titration in the Alkalinity Logbook. This logbook includes, but is not limited to:

14.8.1. Sample preparation and analysis dates.

14.8.2. Sample matrix, initial mass/volume, and final volume.

14.8.3. Ambient temperature.

14.8.4. Initial pH, intermediate pH, and final pH.

14.8.5. Standard lot (or identification) number and concentration.

14.8.6. Titrant volume added.

14.8.7. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.9. Data Interpretation

14.9.1. Quantitation of the target analyte is based on potentiometric titration to the preselected pH.

14.9.1.1. Proper quantitation requires the appropriate selection of an end point from which the alkalinity and the alkalinity relationships can be determined.

14.9.1.2. Determine the phenolphthalein alkalinity as calcium carbonate based on the volume of titrant required to reach pH 8.3. The

formulas for calculating the phenolphthalein alkalinity are listed in Sections 15.4. and 15.5.

14.9.1.3. Determine the total alkalinity as calcium carbonate based on the volume of titrant required to reach the end point. The formulas for calculating the total alkalinity are listed in Sections 15.6., 15.7., and 15.8.

14.9.1.4. Determine the alkalinity relationships based on phenolphthalein alkalinity and total alkalinity. The formulas for calculating the alkalinity relationships are listed in Sections 15.9., 15.10., and 15.11.

14.9.1.5. The molecular weight of calcium carbonate is 100.08 g/mol, and the equivalent weight is 50.04 g/eq. For the calculation of alkalinity, the rounded equivalent weight of 50.0 g/eq is applied for consistency with the formula specified in SM 2320 B.

15. CALCULATIONS

15.1. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.2. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.
Note: Concentrations must be in equivalent units.

15.3. The preparation factor for a solid sample is calculated as follows:

$$P = \frac{V_w}{W_s}$$

where: P = preparation factor for solid sample in mL/g.

V_w = volume of reagent water added for sample preparation in mL. Unless specified otherwise, V_w = 100.
W_s = mass of solid sample used for sample preparation in g.

15.4. The phenolphthalein alkalinity of an aqueous sample is calculated as follows:

$$C_P = \frac{N_{H2SO4} \times V_p \times 50.0 \times 1000}{V_x}$$

where: C_P = phenolphthalein alkalinity of aqueous sample in mg/L of $CaCO_3$.
N_{H2SO4} = normality of sulfuric acid titrant in N.
V_p = volume of sulfuric acid titrant used to reach pH 8.3 in mL.
V_x = volume of aqueous sample titrated in mL.

15.5. The phenolphthalein alkalinity of a solid sample is calculated as follows:

$$C_P = \frac{N_{H2SO4} \times V_p \times 50.0 \times 1000}{V_x} \times P$$

where: C_P = phenolphthalein alkalinity of solid sample in mg/kg of $CaCO_3$.
N_{H2SO4} = normality of sulfuric acid titrant in N.
V_p = volume of sulfuric acid titrant used to reach pH 8.3 in mL.
V_x = volume of supernatant from solid sample titrated in mL.
P = preparation factor for solid sample in mL/g.

15.6. The total alkalinity of an aqueous sample is calculated as follows:

$$C_T = \frac{N_{H2SO4} \times V_f \times 50.0 \times 1000}{V_x}$$

where: C_T = total alkalinity of aqueous sample in mg/L of $CaCO_3$.
N_{H2SO4} = normality of sulfuric acid titrant in N.
V_f = total volume of sulfuric acid titrant used to reach final pH in mL.
V_x = volume of aqueous sample titrated in mL.

15.7. The total alkalinity of an aqueous sample with low alkalinity is calculated as follows:

$$C_T = \frac{N_{H2SO4} \times (2V_i - V_f) \times 50.0 \times 1000}{V_x}$$

where: C_T = total alkalinity of aqueous sample with low alkalinity in mg/L of $CaCO_3$.
N_{H2SO4} = normality of sulfuric acid titrant in N.
V_i = volume of sulfuric acid titrant used to reach intermediate pH in mL.
V_f = total volume of sulfuric acid titrant used to reach final pH in mL.
V_x = volume of aqueous sample titrated in mL.

15.8. The total alkalinity of a solid sample is calculated as follows:

$$C_T = \frac{N_{H2SO4} \times V_f \times 50.0 \times 1000}{V_x} \times P$$

where: C_T = total alkalinity of solid sample in mg/kg of $CaCO_3$.
N_{H2SO4} = normality of sulfuric acid titrant in N.
V_f = total volume of sulfuric acid titrant used to reach final pH in mL.
V_x = volume of supernatant from solid sample titrated in mL.
P = preparation factor for solid sample in mL/g.

15.9. The bicarbonate alkalinity of a sample is calculated as follows:

$$C_B = C_T - 2C_P$$

where: C_B = bicarbonate (HCO_3^-) alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_T = total alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_P = phenolphthalein alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
If $2C_P \geq C_T$, $C_B = 0$.

15.10. The carbonate alkalinity of a sample is calculated as follows:

$$C_C = C_T - C_B - C_H$$

where: C_C = carbonate (CO_3^{2-}) alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_T = total alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_B = bicarbonate (HCO_3^-) alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_H = hydroxide alkalinity of sample in mg/L or mg/kg of $CaCO_3$.

15.11. The hydroxide alkalinity of a sample is calculated as follows:

$$C_H = 2C_P - C_T$$

where: C_H = hydroxide (OH^-) alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
C_P = phenolphthalein alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
If $2C_P \leq C_T$, $C_H = 0$.
C_T = total alkalinity of sample in mg/L or mg/kg of $CaCO_3$.

15.12. All concentrations shall be reported in mg/L (ppm) of alkalinity as $CaCO_3$ for aqueous samples, and mg/kg (ppm) of alkalinity as $CaCO_3$ for soil and solid waste samples.

15.13. Report concentrations which are < 10 mg/L (or mg/kg) to 2 significant figures, and concentrations which are ≥ 10 mg/L (or mg/kg) to 3 significant figures.

15.14. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) or Safety Data Sheets (SDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS or SDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The concentrations of target analytes in an MB should be ≤ ½ the respective reporting limits (RLs). If the concentration of any target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. Both the LCS and the LCSD must be reported.

18.3. The acceptance criteria for duplicate compounds are predetermined. The RPD is ≤ 25%.

18.3.1. When the RPD of the duplicate compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The sample duplicate data shall be reported with the corresponding sample data.

18.3.2. If the RPD of the duplicate compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Matrix effects or poor technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. All concentrations shall be reported in mg/L (ppm) of alkalinity as $CaCO_3$ for aqueous samples, and mg/kg (ppm) of alkalinity as $CaCO_3$ for soil and solid waste samples.

18.7. Report concentrations which are < 10 mg/L (or mg/kg) to 2 significant figures, and concentrations which are ≥ 10 mg/L (or mg/kg) to 3 significant figures.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Director, Project Manager, Quality Control Director, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the group leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *2320 B. Alkalinity, Titration Method*, Approved by Standard Methods Committee, 1997, Editorial Revisions, 2011, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012.

22.2. *2020 B. Quality Control Practices,* Reviewed by Standard Methods Committee, 2010, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012.

22.3. *EPA Method 310.1: Alkalinity (Titrimetric, pH 4.5)*, Editorial Revision 1978, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.4. *Fisher Scientific accumet® Basic AB 15/15+ Bench-Top pH Meter User Manual,* Revision 2, December 2003.

23. APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Procedures for pH Meter and Electrode Calibration and Maintenance.

23.2. Appendix B: Procedure for Sulfuric Acid Titrant Standardization.

23.3. Appendix C: Procedure for DL Determination and LOD Verification Sample Preparation.

23.4. Appendix D: Additional Quality Control Criteria for Department of Defense Projects.

23.5. Appendix E: SM 4500-CO_2 D, Carbon Dioxide by Calculation.

24. ►MODIFICATIONS

24.1. ►The following modifications from SM 2320 B Approved 1997 are noted.

Calscience SOP M738 Section	Reference Document SM 2320 B Section	Summary of Modification
2., 14.4. and 14.7., 15., 18.6., Appendix C, 5. and 6., Appendix E, 8.2.	All	***Method is applied to soil and solid waste samples as a modified method.***

24.2. ►The following modifications from EPA Method 310.1 Editorial Revision 1978 are noted.

Calscience SOP M738 Sections	**Reference Document EPA Method 310.1 Section**	**Summary of Modification**
2., 14.4. and 14.7., 15., 18.6., Appendix C, 5. and 6., Appendix E, 8.2.	***1.0***	***Method is applied to soil and solid waste samples as a modified method.***

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.3	All Sections: Correct minor typos. Section 2: Update matrices. Section 3: Insert reference to RL and DL. Section 6: Add LOD/LOQ definitions. Section 9: Insert reference to pH meter hardware, software, maintenance, and troubleshooting information. Section 11: Update sample container and temperature information. Section 12: Update quality control. Section 13: Update balance calibration check procedure and criteria. Section 14: Update procedure. Section 15: Update calculations. Section 18: Add acceptance criteria to LCS/LCSD. Section 20: Add contingencies to out-of-control LCS/LCSD. Section 22: Update references. Section 24: Revise modifications. Section 25: Add revision history. Appendix B: Revise procedure for titrant standardization. Appendix C: Revise procedure for DL determination and LOD verification. Appendix D: Update DoD quality control requirements and criteria. Appendix E: Revise method references and modifications.	K. Burney / K. Chang	12/10/12

Revision	Description	Author	Effective Date
1.4	Section 6: Update definitions. Section 11: Update sample storage. Section 12: Update QC requirements. Section 18: Update acceptance criteria. Section 22: Update references. Section 25: Update Revision History.	K. Burney	12/16/13
1.5	Entire document: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 12 and 18: Update LCSD requirement. Sections 19 and 20: Update responsibilities.	L. Hunt	03/23/15
1.6	Section 24: Update modifications table.	L. Hunt	04/06/15

Appendix A

PROCEDURES FOR PH METER AND ELECTRODE CALIBRATION AND MAINTENANCE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2320 B / EPA Method 310.1, Alkalinity (Titration Method) – Procedures for pH Meter and Electrode Calibration and Maintenance.

2. SCOPE AND APPLICATIOIN

2.1. The procedures described herein are in addition to the standard procedure.

3. REAGENTS AND STANDARDS

3.1. Reagents

3.1.1. Electrode refilling solution, containing 4-M KCl saturated with AgCl, Fisher Scientific Catalog Number SP135-500 or equivalent.

3.1.2. Electrode storage solution, containing potassium hydrogen phthalate and potassium chloride, Fisher Scientific Catalog Number SE40-1 or equivalent.

3.1.3. Soak solution.

3.1.3.1. Prepare the soak solution by adding the electrode storage solution to equal volume of the pH 7.00 buffer solution.

3.1.3.2. The pH 4.00 buffer solution may be used in place of the pH 7.00 buffer solution if the pH 7.00 buffer solution is unavailable.

3.2. Standards

3.2.1. Calibration

3.2.1.1. Pre-certified and NIST traceable pH 4.00 (color-coded red) buffer solution, in a sealed polypropylene bottle, clear red liquid, containing potassium hydrogen phthalate, is used to calibrate the pH meter and the electrode.

3.2.1.2. Pre-certified and NIST traceable pH 7.00 (color-coded yellow) buffer solution, in a sealed polypropylene bottle, clear yellow liquid, containing potassium phosphate monobasic and sodium hydroxide, is used to calibrate the pH meter and the electrode.

3.2.1.3. Pre-certified and NIST traceable pH 10.00 (color-coded blue) buffer solution, in a sealed polypropylene bottle, clear blue liquid, containing potassium carbonate, potassium borate, potassium hydroxide, and disodium ethylenediaminetetraacetate (EDTA) dihydrate is used to calibrate the pH meter and the electrode.

3.2.2. Calibration Verification

3.2.2.1. Pre-certified and NIST traceable pH 7.00 buffer solution, in a sealed polypropylene bottle, clear colorless liquid, containing potassium phosphate monobasic and sodium hydroxide, is used to verify the pH meter and the electrode calibration.

3.2.2.2. The pH 7.00 buffer must be of a source differing from that used for the calibration. If it is of the same source, then it must be of different lot.

3.2.3. All buffers must be inspected and documented in the Solvent/Standard Verification Logbook prior to use.

4. QUALITY CONTROL

4.1. Calibration

4.1.1. The three-point calibration must be established daily prior to sample analysis and after every batch of 20 samples or portion thereof within a 24-hour shift.

4.1.1.1. The calibration curve is established with pH 4.00, pH 7.00, and pH 10.00 buffers at 25°C.

4.1.2. The calibration is deemed valid if the final percent slope of the electrode is within the specified range.

4.1.2.1. For accumet® Basic pH Meter, the final percent slope of the electrode should be within the range of 90−105%.

4.1.2.2. For accumet® Basic AB 15 Bench-Top pH Meter, the final percent slope of the electrode should be within the range of 90−102%.

4.1.3. If this criterion is not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

4.2. Calibration Verification

4.2.1. The calibration is deemed valid if the measured pH value of the buffer is within 7.00 ± 0.05 pH units at 25°C.

4.2.2. If this criterion is not met, the calibration is deemed unacceptable for sample analysis to begin. An unacceptable calibration verification result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Investigate, effect corrective action, and recalibrate.

5. CALIBRATION AND STANDARDIZATION

5.1. pH Meter and Electrode Calibration

5.1.1. Establish an acceptable three-point calibration curve. The acceptance criterion for the calibration is listed in Section 4.1. of this appendix.

5.1.1.1. Recalibration is required for the following maintenance procedures.

5.1.1.1.1. Clean or replace the electrode.

5.1.1.1.2. Add electrode refilling solution.

5.1.2. After obtaining an acceptable three-point calibration curve and prior to processing environmental or QC samples, the second source buffer must be analyzed to verify the calibration. The acceptance criterion for the calibration verification is listed in Section 4.2. of this appendix.

6. PROCEDURE

6.1. pH Meter and Electrode Setup

6.1.1. Verify that the fill hole of the electrode in the open position.

6.1.1.1. If the fill hole is in the closed position, rotate the blue cap ring clockwise until the fill hole is in the open position.

6.1.2. Verify that the electrolyte level in the reference cavity (outer annular space) of the electrode is sufficiently high.

6.1.2.1. If the electrolyte level is lower than ¼ inch below the cap, add electrode refilling solution.

6.1.3. Verify that the electrode and the ATC probe are connected to the pH meter securely.

6.1.3.1. The pH meter will adjust for varying temperature continuously when the ATC probe is connected. Hence, the measured values of the buffers may vary slightly from the nominal values due to temperature variations.

6.1.3.2. The nominal values of the buffers at various temperatures are as follows:

Temperature (°C)	pH		
	4.00 (± 0.01)	7.00 (± 0.01)	10.00 (± 0.02)
0	4.01	7.13	10.34
5	3.99	7.10	10.26
10	4.00	7.07	10.19
15	3.99	7.05	10.12
20	4.00	7.02	10.06
25	4.00	7.00	10.00
30	4.01	6.99	9.94
35	4.02	6.98	9.90
40	4.03	6.97	9.85
50	4.06	6.97	9.78
60	4.09	6.98	9.70

6.1.3.3. The default temperature of the pH meter is set at 25°C if the ATC probe is not connected.

6.1.4. Verify that the meter screen is in pH mode.

6.1.4.1. For accumet® Basic pH Meter, press and release the "pH/mV" button to toggle between pH, mV, and relative mV (rel mV) modes.

6.1.4.2. For accumet® Basic AB 15 Bench-Top pH Meter, press and release the "mode" button to toggle between pH, mV, and relative mV (REL mV) modes.

6.2. pH Meter and Electrode Calibration

6.2.1. Prepare fresh buffers prior to each calibration.

6.2.2. Clear an existing calibration from the meter memory.

6.2.2.1. For accumet® Basic pH Meter, press the "Setup" button once. When the meter screen displays a flashing "Clear Buffers" icon, press the "Enter" button to clear all existing buffers.

6.2.2.2. For accumet® Basic AB 15 Bench-Top pH Meter, press the "setup" button twice. When the meter screen displays the "clear BUFFER" icon, press the "enter" button to clear all existing buffers.

6.2.3. Calibrate the meter and the electrode using fresh buffers in the order presented. Bad calibration sequence technique will cause electrode error.

6.2.3.1. Rinse the electrode with reagent water and blot dry with a tissue wiper.

6.2.3.2. Immerse the electrode in the pH 7.00 buffer to cover both the glass pH sensing bulb and the reference junction.

6.2.3.2.1. The electrolyte level in the reference cavity should be above the buffer level to prevent reverse electrolyte flow.

6.2.3.3. Press the appropriate button to calibrate.

6.2.3.3.1. For accumet® Basic pH Meter, press the "Standardize" button. When the reading is stable, press the "Enter" button.

6.2.3.3.2. For accumet® Basic AB 15 Bench-Top pH Meter, press the "std" button. When the reading is stable, press the "std" button.

6.2.3.4. Repeat Sections 6.2.3.1. through 6.2.3.3. of this appendix using the pH 4.00 buffer.

6.2.3.5. Repeat Sections 6.2.3.1. through 6.2.3.3. of this appendix using the pH 10.00 buffer.

6.2.3.6. Record the final percent slope to the nearest 1%.

6.2.4. If the meter screen displays "electrode error" message during calibration, the electrode may be dirty or damaged, or the buffer(s) may be contaminated. Perform the following corrective actions and recalibrate.

6.2.4.1. Clean or replace the electrode, or change the buffer(s).

6.2.4.2. Proceed to Sections 6.2.2. and 6.2.3. of this appendix to clear the existing calibration from the meter memory and recalibrate.

6.2.4.3. If the "electrode error" message persists, remove the pH meter from service.

6.2.5. Verify the calibration using a fresh second source pH 7.00 buffer.

6.2.5.1. Rinse the electrode with reagent water and blot dry with a tissue wiper.

6.2.5.2. Immerse the electrode in the second source pH 7.00 buffer to cover both the glass pH sensing bulb and the reference junction.

6.2.5.2.1. The electrolyte level in the reference cavity should be above the buffer level to prevent reverse electrolyte flow.

6.2.5.3. When the reading is stable, record the pH to the nearest 0.01 pH unit.

6.2.5.3.1. For accumet® Basic pH Meter, the meter screen displays the "S" icon when the reading is stable.

6.2.5.3.2. For accumet® Basic AB 15 Bench-Top pH Meter, the meter screen displays the "STABLE" icon when the reading is stable.

6.3. New Electrode Preparation

6.3.1. Carefully remove a new electrode from the storage bottle according to manufacturer's instructions to prevent damage to the electrode.

6.3.2. Visually inspect the glass pH sensing bulb for cracks and scratches.

6.3.3. Rinse the sensing part of the electrode with warm (60–80°C) distilled or deionized water.

6.3.4. Rotate the blue cap ring clockwise until the fill hole of the electrode is in the open position.

6.3.5. Check the electrolyte level in the reference cavity (outer annular space) of the electrode.

6.3.5.1. If the electrolyte level is not visible, the electrode may be filled to capacity just beneath the cap.

6.3.5.2. If the electrolyte level is lower than ¼ inch below the cap, add electrode refilling solution.

6.3.6. Connect the electrode and the ATC probe to the pH meter securely.

6.3.7. Immerse the electrode in the soak solution for 5–10 minutes prior to calibration.

6.3.8. Document the serial number of the electrode and the placed-in-service date in the Instrument Maintenance Logbook. Retain the test certificate of the electrode for reference.

6.4. Electrode Maintenance

6.4.1. Immerse the electrode in the soak solution between measurements.

6.4.2. Keep the fill hole of the electrode in the open position at all times to prevent backflow of the soak solution into the electrode.

6.4.2.1. If long-term storage is anticipated, rotate the blue cap ring counterclockwise until the fill hole of the electrode is in the close position. Return the electrode to the storage bottle according to manufacturer's instructions to prevent damage to the electrode.

6.4.3. Check the reference junction of the electrode for blockage. Symptoms of blocked or clogged reference junctions are extremely slow response, off-scale readings, and/or electrically noisy measurements.

6.4.3.1. Replace the screw cap of the electrode refilling solution bottle with the spout cap.

6.4.3.2. Extend the spout and press it firmly into the fill hole of the electrode to create an airtight seal.

6.4.3.3. Gently squeeze the electrode refilling solution bottle until a bead of liquid forms at the reference junction.

6.4.3.3.1. If no bead is observed, drain the electrolyte. Rinse the reference cavity with distilled or deionized water and refill with fresh electrolyte.

6.4.3.4. Immerse the electrode in the soak solution for 5–10 minutes prior to calibration.

6.4.4. Clean the glass membrane of the electrode as often as needed. Symptoms of dirty glass membrane are slow response, noisy, unstable, or erratic readings.

6.4.4.1. Rinse the sensing part of the electrode with warm (60–80°C) distilled or deionized water.

6.4.4.2. Immerse the electrode in the soak solution for 5–10 minutes prior to calibration.

Appendix B

PROCEDURE FOR SULFURIC ACID TITRANT STANDARDIZATION

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2320 B / EPA Method 310.1, Alkalinity (Titration Method) – Procedure for Sulfuric Acid Titrant Standardization.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

3. REAGENTS AND STANDARDS

3.1. Reagents

3.1.1. Sodium carbonate, Na_2CO_3, anhydrous, 105.99 molecular weight (or 53.00 equivalent weight), white powder, certified, reagent grade or equivalent.

3.1.1.1. Dry 3–5 g of sodium carbonate by baking at 250°C for 4 hours on a watch glass, and cool in a desiccator.

3.1.2. All reagents must be inspected and documented in the Solvent/Standard Verification Logbook prior to use.

3.2. Standards

3.2.1. Manually-prepared stock standard solutions, in sealed volumetric flasks, containing sodium carbonate in reagent water, are used to standardize H_2SO_4 stock standard solutions.

3.2.1.1. Prepare the 0.02-N Na_2CO_3 stock standard solution by dissolving 0.2650 ± 0.0001 g of anhydrous Na_2CO_3 in 250 mL of carbon dioxide free reagent water. Record the exact mass of anhydrous Na_2CO_3 used to the nearest 0.0001 g.

3.2.1.2. Prepare the 0.1-N Na_2CO_3 stock standard solution by dissolving 1.3249 ± 0.0001 g of anhydrous Na_2CO_3 in 250 mL of carbon dioxide free reagent water. Record the exact mass of anhydrous Na_2CO_3 used to the nearest 0.0001 g.

3.2.1.3. The Na_2CO_3 stock standard solutions must be prepared fresh prior to standardization.

3.2.2. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

4. PROCEDURE

4.1. Measure the appropriate volume of the Na_2CO_3 stock standard solution into a clean beaker containing approximately 25 mL of reagent water and one stir bar.

4.1.1. To standardize the 0.02-N H_2SO_4 stock standard solution, measure exactly 25.0 mL of the 0.02-N Na_2CO_3 stock standard solution.

4.1.2. To standardize the 0.1-N H_2SO_4 stock standard solution, measure exactly 25.0 mL of the 0.1-N Na_2CO_3 stock standard solution.

4.2. Place the beaker on a magnetic stirrer. Set the magnetic stirrer to stir gently.

4.3. Immerse the electrode in the Na_2CO_3 solution to cover both the glass pH sensing bulb and the reference junction.

4.4. Titrate potentiometrically to pH of about 5 with the magnetic stirrer operating.

4.5. Remove the electrode from the solution and rinse the electrode with reagent water into the same beaker.

4.6. Place the beaker on a hot plate, cover with a watch glass, and boil gently for 3 to 5 minutes.

4.7. Cool the solution to ambient (room) temperature, and rinse the watch glass with reagent water into the same beaker.

4.8. Place the beaker on a magnetic stirrer. Set the magnetic stirrer to stir gently.

4.9. Immerse the electrode in the solution to cover both the glass pH sensing bulb and the reference junction.

4.10. Titrate potentiometrically to pH 4.5 with the magnetic stirrer operating.

4.11. Record the total volume of the sulfuric acid titrant used to the nearest 0.1 mL.

4.12. Calculate the normality of the sulfuric acid titrant. The formula for calculating normality is listed in Section 5.1. of this appendix. Record the calculated normality to 2 significant figures.

5. CALCULATIONS

5.1. The normality of sulfuric acid titrant is calculated as follows:

$$N_{H2SO4} = \frac{M_{Na2CO3}}{0.25 \times 53.00} \times \frac{V_{Na2CO3}}{V_{H2SO4}}$$

where: N_{H2SO4} = normality of sulfuric acid titrant in N.
M_{Na2CO3} = mass of anhydrous sodium carbonate used to prepare 250-mL sodium carbonate stock standard solution in g.
V_{Na2CO3} = volume of sodium carbonate stock standard solution used in mL. Unless specified otherwise, V_{Na2CO3} = 25.0.
V_{H2SO4} = volume of sulfuric acid titrant used in mL.

5.2. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

Appendix C

PROCEDURE FOR DL DETERMINATION AND LOD VERIFICATION SAMPLE PREPARATION

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2320 B / EPA Method 310.1, Alkalinity (Titration Method) – Procedure for DL Determination and LOD Verification Sample Preparation.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

3. REAGENTS

3.1. Sodium carbonate, Na_2CO_3, anhydrous, 105.99 molecular weight (or 53.00 equivalent weight), white powder, certified, reagent grade or equivalent.

3.1.1. Dry 3–5 g of sodium carbonate by baking at 250°C for 4 hours on a watch glass, and cool in a desiccator.

3.2. Calcium carbonate, $CaCO_3$, 100.09 molecular weight (or 50.04 equivalent weight), white powder, certified, reagent grade or equivalent.

3.3. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

4. EQUIPMENT AND SUPPLIES

4.1. Volumetric flasks, 100 mL and 1000 mL, glass, Class A.

5. PROCEDURE

5.1. Aqueous DL Determination Sample Preparation

5.1.1. Prepare each DL determination sample as follows:

5.1.1.1. Measure exactly 100 mL of carbon dioxide free reagent water into a clean specimen container containing a stir bar.

5.1.1.2. Dissolve the appropriate mass of Na_2CO_3 in the carbon dioxide free reagent water.

5.1.1.2.1. The appropriate mass is derived from the expected concentration of the DL determination sample. The formula for calculating the appropriate mass is listed in Section 6.1. of this appendix.

5.1.2. Prepare seven DL determination samples and proceed to potentiometric titration of low alkalinity procedure.

5.2. Aqueous LOD Verification Sample Preparation

5.2.1. Prepare the LOD verification sample as follows:

5.2.1.1. Measure exactly 100 mL of carbon dioxide free reagent water into a clean specimen container containing a stir bar.

5.2.1.2. Dissolve the appropriate mass of Na_2CO_3 in the carbon dioxide free reagent water.

5.2.1.2.1. The appropriate mass is derived from the calculated DL value. The formula for calculating the appropriate mass is listed in Section 6.2. of this appendix.

5.2.2. Proceed to potentiometric titration of low alkalinity procedure.

5.3. Solid DL Determination Sample Preparation

5.3.1. Prepare the Na_2CO_3 solution by dissolving 0.0106 ± 0.0001 g of Na_2CO_3 in carbon dioxide free reagent water and dilute to 100 mL with additional carbon dioxide free reagent water.

5.3.2. Prepare each DL determination sample as follows:

5.3.2.1. Measure exactly 20.0 g of washed sea sand into a clean specimen container.

5.3.2.2. Add the appropriate volume of the Na_2CO_3 solution (1.00-mL = 0.1-mg $CaCO_3$) into the sand.

5.3.2.2.1. The appropriate volume is derived from the expected concentration of the DL determination sample. The formula for calculating the appropriate volume is listed in Section 6.3. of this appendix.

5.3.2.3. Add sufficient amount of carbon dioxide free reagent water to bring the final volume of the liquid phase to 100 mL.

5.3.2.4. Measure 50 ± 1 mL of the supernatant into a clean specimen container containing a stir bar.

5.3.3. Prepare seven MDL study samples and proceed to potentiometric titration procedure.

5.4. Solid LOD Verification Sample Preparation

5.4.1. Prepare the Na_2CO_3 solution by dissolving 0.0106 ± 0.0001 g of Na_2CO_3 in carbon dioxide free reagent water and dilute to 100 mL with additional carbon dioxide free reagent water.

5.4.2. Prepare the LOD verification sample as follows:

5.4.2.1. Measure exactly 20.0 g of washed sea sand into a clean specimen container.

5.4.2.2. Add the appropriate volume of the Na_2CO_3 solution (1.00 mL = 0.1 mg $CaCO_3$) into the sand.

5.4.2.2.1. The appropriate volume is derived from the calculated DL value. The formula for calculating

the appropriate volume is listed in Section 6.4. of this appendix.

5.4.2.3. Add sufficient amount of carbon dioxide free reagent water to bring the final volume of the liquid phase to 100 mL.

5.4.2.4. Measure 50 ± 1 mL of the supernatant into a clean specimen container containing a stir bar.

5.4.3. Proceed to potentiometric titration procedure.

6. CALCULATIONS

6.1. The mass of sodium carbonate required for aqueous DL determination sample preparation is calculated as follows:

$$M_{Na2CO3} = C_{DL} \times V_{DL} \times \frac{105.99}{100.09}$$

where: M_{Na2CO3} = mass of sodium carbonate used to prepare DL determination sample in mg.
C_{DL} = expected concentration of DL determination sample in mg/L of $CaCO_3$.
V_{DL} = volume of DL determination sample in L.
Unless specified otherwise, V_{DL} = 0.100.

6.2. The mass of sodium carbonate required for aqueous LOD verification sample preparation is calculated as follows:

$$M_{Na2CO3} = C_{DL} \times V_{LOD} \times \frac{105.99}{100.09} \times 2$$

where: M_{Na2CO3} = mass of sodium carbonate used to prepare LOD verification sample in mg.
C_{DL} = calculated DL value in mg/L of $CaCO_3$.
V_{LOD} = volume of LOD verification sample in L.
Unless specified otherwise, V_{LOD} = 0.100.

6.3. The volume of sodium carbonate solution required for solid DL determination sample preparation is calculated as follows:

$$V_{Na2CO3} = \frac{C_{DL} \times M_{DL}}{0.1}$$

where: V_{Na2CO3} = volume of sodium carbonate solution used to prepare DL determination sample in mL.
C_{DL} = expected concentration of DL determination sample in mg/kg of $CaCO_3$.
M_{DL} = mass of DL determination sample in kg.

Unless specified otherwise, M_{DL} = 0.0200.

6.4. The volume of sodium carbonate solution required for solid LOD verification sample preparation is calculated as follows:

$$V_{Na2CO3} = \frac{C_{DL} \times M_{LOD}}{0.1} \times 2$$

where: V_{Na2CO3} = volume of sodium carbonate solution used to prepare LOD verification sample in mL.
C_{DL} = calculated DL value in mg/kg of $CaCO_3$.
M_{LOD} = mass of LOD verification sample in kg.
Unless specified otherwise, M_{LOD} = 0.0200.

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2320 B / EPA Method 310.1, Alkalinity (Titration Method) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

4.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

4.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. No samples shall be analyzed without a valid LOD.

4.2. Limit of Quantitation (LOQ)

4.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

4.3. Event Based Quality Control (MBs and LCS/LCSDs)

4.3.1. Method Blanks (MBs)

4.3.1.1. The MB is considered to be contaminated if one of the following conditions is met.

4.3.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.3.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

4.3.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

4.3.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

4.3.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.3.2. Laboratory Control Samples (LCS/LCSDs)

4.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

4.3.2.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5. REFERENCES

5.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix E

SM 4500-CO_2 D, CARBON DIOXIDE BY CALCULATION

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 4500-CO_2 D, Carbon Dioxide by Calculation.

2. DETECTION / QUANTITATION LIMITS

2.1. The reporting limits (RLs) for this method are as follows:

Carbon Dioxide Concentration (mg/L or mg/kg)	Aqueous EQL (mg/L)	Solid EQL (mg/kg)
C < 100	1.0	5.0
100 ≤ C < 1000	5.0	5.0
1000 ≤ C < 10000	10.0	10.0
10000 ≤ C < 100000	100	100
C ≥ 100000	1000	1000

Note: C = Free Carbon Dioxide

3. SCOPE AND APPLICATION

3.1. When the total alkalinity (SM 2320 B) of a water is due almost entirely to hydroxides, carbonates, or bicarbonates, and the total dissolved solids (SM 2540 C) is not greater than 500 mg/L, the free CO_2 can be calculated from the sample pH and total alkalinity.

3.1.1. The calculation is subject to the accuracy of the sample pH and total alkalinity determined at 25°C.

4. METHOD SUMMARY

4.1. SM 4500-CO_2 D is used to calculate free carbon dioxide from the sample pH and bicarbonate alkalinity.

5. INTERFERENCES

5.1. The error resulting from inaccurate pH measurements grows with an increase in total alkalinity.

5.1.1. For example, an inaccuracy of 0.1 in the pH determination causes a CO_2 error of 2 to 4 mg/L in the pH range of 7.0 to 7.3 and a total alkalinity of 100 mg/L $CaCO_3$. In the same pH range, the error approaches 10 to 15 mg/L when the total alkalinity is 400 mg/L $CaCO_3$.

5.2. Some treatment processes, such as superchlorination and coagulation, can affect significantly pH and total-alkalinity values of a poorly buffered water of low alkalinity and low total-dissolved-mineral content.

6. EQUIPMENT AND SUPPLIES

6.1. Calculator, Scientific, Sper Scientific Calculator Model 830005 or equivalent.

7. PROCEDURE

7.1. If it is required, verify that the total dissolved solids is not greater than 500 mg/L via the procedure as outlined in SM 2540 C (refer to SOP-M713).

7.2. Determine the pH via the procedure as outlined in SM 4500-H^+ B, EPA Method 9040C, or EPA Method 9045D (refer to SOP-M739 or SOP-M736).

7.3. Determine the bicarbonate alkalinity via the procedure as outlined in SM 2320 B (refer to this SOP).

7.4. Data Interpretation

7.4.1. Determine the free carbon dioxide from the pH and bicarbonate alkalinity. The formula for calculating the free carbon dioxide is listed in Section 8.1. of this appendix.

8. CALCULATIONS

8.1. The free carbon dioxide of a sample is calculated as follows:

$$C_D = 2.0 \times C_B \times 10^{(6-pH)}$$

where: C_D = free carbon dioxide of sample in mg/L or mg/kg of CO_2.
C_B = bicarbonate (HCO_3^-) alkalinity of sample in mg/L or mg/kg of $CaCO_3$.
pH = pH value of sample in pH unit.

8.2. All concentrations shall be reported in mg/L (ppm) of free carbon dioxide as CO_2 for aqueous samples, and mg/kg (ppm) of free carbon dioxide as CO_2 for soil and solid waste samples.

8.3. Report concentrations which are < 10 mg/L (or mg/kg) to 2 significant figures, and concentrations which are ≥ 10 mg/L (or mg/kg) to 3 significant figures.

8.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

9. REFERENCES

9.1. *4500-CO_2 D. Carbon Dioxide and Forms of Alkalinity by Calculation*, Approved by Standard Methods Committee, 1997, Editorial Revisions, 2011, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012.

10. MODIFICATIONS

10.1. The following modifications from SM 4500-CO_2 D Approved 1997 are noted.

Calscience SOP M738 Section	**Reference Document SM 4500-CO_2 D Section**	**Summary of Modification**
7.3. (Appendix E)	2d	Bicarbonate alkalinity is determined via the procedure as outlined in SM 2320 B.

Title : **SM 2540C / EPA METHOD 160.1, TOTAL DISSOLVED SOLIDS (FILTERABLE RESIDUE, GRAVIMETRIC)**

Document No. : SOP-M713
Revision No. : 2.8
Supersedes : 2.7

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PROPRIETARY INFORMATION STATEMENT

Revision 2.8 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ **MANAGEMENT** 03/20/15 **DATE**

_____ **QA DEPARTMENT** 03.20.15 **DATE**

Reviewer Signature	Review Date	Comments	QA Signature
	02/22/16		

1. METHOD IDENTIFICATION

1.1. SM 2540C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, Gravimetric).

2. APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface and saline waters, domestic and industrial wastewaters.

2.2. Soil, solid, and non-aqueous matrices may be analyzed using the extraction procedure noted in Section 14.5. and reporting as a modified method, EPA Method 160.1(M) or SM 2540C(M).

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Concentration (mg/L or mg/kg) in Sample	EQL (mg/L or mg/kg)
≤ 999	1.0
> 999 and ≤ 9,999	10
> 9,999 and ≤ 99,999	100
> 99,999	1000

4. SCOPE AND APPLICATION

4.1. SM 2540C / EPA Method 160.1 are used to determine the total dissolved solids.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of the equipment and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

4.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated in weighed beaker and dried to a constant weight at 180°C. The increase in weight of the beaker represents the total dissolved solids.

5.2. The filtrate from the determination of total suspended solids (non-filterable residue) may be used for this method.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1 %.

6.10. Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of

the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.15. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.22. Terms Specific to Solids Analysis

6.22.1. Total Dissolved Solids: The portion of total solids that passes through a filter of 2.0 µm (or smaller) nominal pore size under specified conditions.

6.22.2. Total Solids: Material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include total dissolved solids and total suspended solids.

6.22.3. Total Suspended Solids: The portion of total solids retained on a filter of 2.0 µm nominal pore size under specified conditions.

6.23. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling.

7.1.1. Mix small samples with a magnetic stirrer. Avoid using a magnetic stirrer if the samples contain magnetic particles.

7.1.2. If suspended solids are present, pipet with wide-bore pipets.

7.1.3. If part of a sample adheres to the sample container, document it in the logbook when evaluating and reporting results.

7.2. Some samples may dry with the formation of a crust that prevents water evaporating.

7.2.1. Limit sample to no more than 200 mg residue to prevent water-trapping crust.

7.3. Weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, gases from heat-induced chemical decomposition, and weight gains due to oxidation depend on the temperature and heating time at which the residue is dried.

7.3.1. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator to prevent moist air from entering.

7.3.2. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

7.4. Residue dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of carbon dioxide may convert bicarbonate to carbonate, and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost.

7.4.1. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained from summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

7.5. Residues high in oil or grease may yield questionable results because of the difficulty of drying to constant weight in a reasonable time.

7.5.1. Disperse visible floating oil and grease with a blender before withdrawing a sample aliquot for analysis.

7.6. Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

7.7. Samples containing high concentrations of bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate.

8. ►SAFETY

8.1. Beakers are heated in an oven and will be hot upon removal. Use tongs to handle the weighing dishes when removing from the oven.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Specimen containers, 4.5 oz (120 mL), with lids, high density polyethylene (HDPE) or polypropylene, disposable.

9.2. Graduated cylinders, 25 mL, 50 mL, 100 mL, or other capacity, glass, Class A.

9.2.1. Class A graduated cylinder is utilized to measure sample volume.

9.3. Graduated cylinders, 50 mL, glass, Class B.

9.3.1. Class B graduated cylinder is utilized to collect sample filtrate.

9.4. Volumetric flasks, 1 L, Class A.

9.5. Blender or homogenizer.

9.6. Magnetic stirrer.

9.7. Stir bars, Teflon coated.

9.8. Stir bar retriever, magnetic.

9.9. Transfer pipets, wide-bore, glass or plastic, disposable.

9.10. Spatula, stainless steel.

9.11. Vacuum filtration apparatus:

9.11.1. Vacuum apparatus.

9.11.2. Buchner funnel, 100 mm diameter, 320 mL capacity, porcelain with fixed perforated plate, capable of supporting a 90-mm diameter filter, CoorsTek Fixed Plate Buchner Funnel or equivalent.

9.11.3. Filtration flask, 1000 mL or other capacity, glass, with tubulation.

9.11.4. Filter paper, 1.5 µm effective pore size, 90 mm diameter, borosilicate glass microfiber, binder free, Whatman Grade 934-AH Glass Microfiber Filter or equivalent.

9.12. Ultrasonic bath, VWR Scientific Aquasonic Model 550T or equivalent.

9.13. Drying oven, thermostatically controlled, forced draft, capable of maintaining 180 ± 2°C.

9.14. Hot plate, capable of maintaining 80–100°C.

9.15. Muffle furnace, capable of maintaining 550 ± 50°C.

9.16. Instrument Software

9.16.1. Not applicable.

9.17. Instrument Maintenance and Troubleshooting

9.17.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.17.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.18. Thermometer, calibrated, capable of monitoring temperatures at 90 ± 10°C and 180 ± 2°C.

9.19. Desiccator, containing indicating-type desiccant.

9.20. Forceps or tongs, stainless steel.

9.21. Gloves, heat resistant.

9.22. Wash bottle, 500 mL, 1000 mL, or other capacity, low density polyethylene (LDPE).

9.23. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.24. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.25. Beakers, 100 mL or 150 mL, glass.

9.26. Paper towels.

9.27. Tray, plastic.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, deionized.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium chloride, NaCl, white crystalline solid, reagent grade or equivalent.

10.1.4. All reagents (except reagent water) must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Sodium chloride stock standard solution, 1000 ppm.

10.2.1.1. Dissolve 1.0000 ± 0.0100 g NaCl in reagent water and dilute to 1 L in a volumetric flask.

10.2.2. Sodium chloride working solution, 100 ppm

10.2.2.1. Measure 100 mL of the 1000 ppm NaCl stock solution with a graduated cylinder and dilute to 1 L in a volumetric flask.

10.2.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1 L pre-cleaned high density polyethylene (HDPE) or clear glass containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.2. Solid samples should be collected in 4 oz or 8 oz pre-cleaned clear glass wide-mouth jars (preferable), or 6 in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Samples should be maintained in a chilled state, 0-6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions.

11.3.1. Aqueous and solid samples shall be analyzed as soon as feasible to minimize microbiological decomposition of solids. The maximum holding time is within 7 days of sample collection.

11.4. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. Event Based Quality Control (MBs and LCS/LCSDs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample (LCS) and, in some cases, a laboratory control sample duplicate (LCSD).

12.1.1.1. When requested by client, to meet project DQOs, or if insufficient sample volume is received for a sample duplicate, a laboratory control sample duplicate (LCSD) is required.

12.1.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.1.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. When an LCSD is prepared and analyzed, the RPD is ≤ 20%.

12.1.3. The concentration of target analyte in an MB should be ≤ ½ the respective reporting limit (RL). If the concentration of target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated.

12.2. Matrix Based Quality Control (Sample Duplicates)

12.2.1. Matrix based quality control consists of QC samples processed using actual environmental samples. This consists of a sample duplicate.

12.2.1.1. A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples.

12.2.1.2. A sample duplicate shall be analyzed for every 10 samples or portion thereof.

12.2.2. The acceptance criteria for duplicate analyte are as follows:

12.2.2.1. The RPD is ≤ 5%.

12.2.2.1.1. For EPA Region 9 requirement, the RPD is < 20%.

12.2.2.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

12.2.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

12.3. If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.4. Additional information regarding internal quality control check is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Top Loading Balance

13.2.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.2.2. If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.3. Thermometer

13.3.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

14. PROCEDURE

14.1. Conductivity Determination

14.1.1. Determine the conductivity of an aqueous sample as outlined in the current revision of SOP-M702. Record the conductivity to 3 significant figures in the Total Dissolved Solids Logbook.

14.1.2. Conductivity measurement is used to estimate the concentration (in mg/L) of total dissolved solids in an aqueous sample by multiplying conductivity (in µmho/cm) by an empirical factor. This factor may vary from 0.55 to 0.90, depending on the soluble components of the water and on the temperature of measurement.

14.1.2.1. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide of free acid is present.

14.1.2.2. The factor of 0.6 is applied to all aqueous samples received at the laboratory.

14.2. Beaker Preparation

14.2.1. Using a fine point Sharpie, write an identification number on a clean 100 mL beaker.

14.2.1.1. Handle beaker using clean forceps or tongs throughout the course of beaker preparation.

14.2.1.2. Do not use fingers. Oils or other contaminants from fingers or gloves may change the mass of the beaker and skew the mass of the residue.

14.2.2. Heat the clean, labeled beaker in an oven at 180°C ± 2°C for one hour.

14.2.2.1. If volatile solids are to be measured, heat the beaker in a muffle furnace at 550°C ± 50°C for 15 minutes instead.

14.2.3. Remove the beaker from the oven, transfer to a desiccator, and allow to cool.

14.2.4. When cool to ambient temperature, and immediately prior to sample preparation, weigh the beaker on a calibrated analytical balance. Record the beaker identification number and the mass to the nearest 0.1 mg (or 0.0001 g).

14.2.4.1. Shut all access doors on the balance and tare. Open a single access door, remove a beaker from the desiccator, and place on the balance pan. Shut the access door and allow the digital readout to stabilize before recording the mass.

14.2.4.2. Place the beaker in a tray lined with clean paper towels for immediate use.

14.3. Filter Paper Preparation

14.3.1. If total suspended solids is to be determined in conjunction with this method, prepare filter paper as outlined in the current revision of SOP-M714.

14.4. Aqueous Sample Preparation

14.4.1. Allow an aqueous sample to reach ambient temperature.

14.4.2. Homogenize the aqueous sample by shaking the sample thoroughly. Invert the sample container at least three times while shaking.

14.4.2.1. Sample may be homogenized by stirring with a magnetic stirrer at a speed to shear large particles.

14.4.3. Quickly measure 20.0 ± 1.0 mL of the homogenized aqueous sample into a Class A graduated cylinder. Excess volume may be removed with a disposable transfer pipet. Record the volume to the nearest 0.1 mL or 3 significant figures.

14.4.3.1. For MB, measure exactly 20.0 mL of clean reagent water.

14.4.3.2. For LCS/LCSD, measure exactly 20.0 mL of 100 ppm NaCl working solution.

14.4.3.3. The sample volume shall yield between 2.5 mg and 200 mg dried residue. If the volume filtered fails to meet the minimum yield, increase the sample volume. If complete filtration takes

more than 10 minutes, increase the filter diameter or decrease the sample volume.

14.4.4. Proceed to Section 14.6. for filtration procedure.

14.5. Solid Sample Preparation

14.5.1. Allow a solid sample to reach ambient temperature.

14.5.2. Homogenize the solid sample as outlined in the current revision of SOP-M230.

14.5.3. Measure 3.00 ± 0.15 g of the homogenized solid sample into a clean specimen container. Record the mass to the nearest 0.01 g or 3 significant figures.

14.5.3.1. For MB, measure exactly 3.00 g of washed sea sand. Record the washed sea sand identification number.

14.5.3.2. For LCS/LCSD, measure exactly 3.00 g of washed sea sand. Record the washed sea sand identification number.

14.5.3.2.1. Spike the sand with 2.0 mL of 1000 ppm NaCl stock solution.

14.5.3.3. The sample mass shall yield between 2.5 mg and 200 mg dried residue. If complete filtration takes more than 10 minutes, increase the filter diameter or decrease the sample mass.

14.5.4. Add 20.0 mL of clean reagent water to the solid sample. Cap the specimen container and shake vigorously.

14.5.5. Place the specimen container in an ultrasonic bath, and sonicate the solid sample for at least 30 minutes.

14.5.6. Proceed to Section 14.6. for filtration procedure.

14.6. Assemble a vacuum filtration apparatus with a clean filtration flask and Buchner funnel.

14.7. Place a filter paper in the Buchner funnel and apply vacuum.

14.7.1. Handle filter paper using clean forceps throughout the course of sample preparation and analysis.

14.8. Using wash bottle, wet the filter paper with a small volume of reagent water to seat it on the funnel, then rinse the filter paper with three successive 20 mL portions of reagent water.

14.8.1. If the filter paper was pre-prepared for the determination of total suspended solids, no rinsing with three successive 20 mL portions of reagent water is required.

14.9. Continue to apply vacuum until all traces of water have been removed. Turn the vacuum pump off and discard the washings.

14.10. Place a clean, dry 50 mL Class A or B graduated cylinder in the filtration flask to collect filtrate.

14.11. Apply vacuum and carefully decant the measured sample onto and through the filter paper without splashing. Continue filtration with the vacuum operating.

14.12. Using wash bottle, rinse the filter paper thoroughly with three successive 10 mL portions of reagent water. Allow complete drainage between washings, and continue to apply vacuum for about 3 minutes after filtration is complete or until all visible water is removed.

14.13. Turn the vacuum pump off. Carefully remove the graduated cylinder from the filtration flask using clean forceps or tongs.

14.13.1. Do not splash or spill the contents of the graduated cylinder.

14.14. Pour the filtrate (with washings) into a pre-weighed beaker.

14.14.1. Handle beaker using clean forceps or tongs throughout the course of sample preparation and analysis.

14.15. Place the beaker on a hot plate set at 80–100°C.

14.15.1. Monitor the hot plate temperature with a calibrated thermometer.

14.16. Evaporate the filtrate on the hot plate until all traces of water have been removed.

14.16.1. Evaporating on a hot plate ensures observation that no sample splattering occurs.

14.17. Once dry, transfer the beaker to an oven designated for the analysis.

14.17.1. Check the oven temperature prior to placing the beaker inside. The acceptable temperature range is 178–182°C.

14.17.2. Check the temperature log and/or the actual thermometer to be sure the oven is in proper working condition.

14.18. Dry the residue in the oven at 180 ± 2°C for at least one hour.

14.19. Remove the beaker from the oven, transfer to a desiccator and allow to cool.

14.20. When cool to ambient temperature, weigh the beaker including the dried residue on a calibrated analytical balance. Record the mass to the nearest 0.1 mg (or 0.0001 g).

14.20.1. Repeat the drying cycle (Section 14.18. to Section 14.19.) until a constant mass is obtained. The mass change shall be less than 4% of the previous mass or 0.5 mg, whichever is less.

14.21. Samples are filtered one at a time in the following or other logical order:

1) Method Blank (MB)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD), if required
4) Samples (up to 10, excluding QC)
5) Sample Duplicate
6) Samples (up to 10, excluding QC)
7) Sample Duplicate

14.21.1. Item 1: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.21.1.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.

14.21.1.2. One MB is required every day preparatory procedures (i.e., filtrations, dryings, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.21.2. Item 2: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.21.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.21.2.2. One LCS is required every day sample preparations are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.21.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.

14.21.4. Items 4 and 6: Up to a total of 20 field samples per batch.

14.21.5. Items 5 and 7: The sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.

14.21.5.1. The purpose of the sample duplicate is to access the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.

14.21.5.2. One sample duplicate is required for every 10 samples per matrix or portion thereof processed concurrently.

14.21.5.2.1. For EPA Region 9 requirement, one sample duplicate is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.22. Thoroughly document all aspects of the preparatory procedures in the Total Dissolved Solids Logbook. This logbook includes, but is not limited to:

14.22.1. Preparation and analysis dates.

14.22.2. Sample volume or mass.

14.22.3. Beaker and dried residue masses.

14.22.4. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.23. Data Interpretation

14.23.1. Determine the total dissolved solids of a sample from the sample volume or mass, and the beaker masses before and after sample filtration. The formulas for calculating the concentration of total dissolved solids are listed in Section 15.3. and Section 15.4.

15. CALCULATIONS

15.1. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of total dissolved solids in measurement 1.
C_2 = concentration of total dissolved solids in measurement 2.

Note: Concentrations must be in equivalent units.

15.2. The preparation factor for a solid sample is calculated as follows:

$$P = \frac{V_w}{W_S}$$

where: P = preparation factor for solid sample in mL/g.
V_w = volume of reagent water used prior to sonication in mL. Unless specified otherwise, V_w = 20.
W_S = mass of solid sample sonicated in g.

15.3. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_A}$$

where: C_{TDS} = concentration of total dissolved solids (TDS) in mg/L.
M_f = mass of beaker and oven-dried residue in mg.
M_i = mass of beaker in mg.
V_A = volume of aqueous sample filtered in mL.

15.4. The target analyte concentration for a solid sample is calculated as follows:

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_x} \times P$$

where: C_{TDS} = concentration of total dissolved solids (TDS) in mg/kg.
M_f = mass of beaker and oven-dried residue in mg.
M_i = mass of beaker in mg.
V_x = volume of sonicated solid sample filtered in mL. Unless specified otherwise, V_x = 20.
P = preparation factor for solid sample in mL/g.

15.5. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

15.6. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥ 100 ppm to 3 significant figures.

15.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of ***Eurofins*** Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The concentration of target analyte in an MB should be ≤ ½ the respective reporting limit (RL). If the concentration of target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD (when applicable) is within acceptance limits, and all target analytes in

the associated samples are not detected, the sample data can be reported without qualification.

18.2.2. If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.

18.3. The acceptance criteria for duplicate analyte are predetermined. The RPD is ≤ 5%.

18.3.1. For EPA Region 9 requirement, refer to Section 12.2.2.1.1. for acceptance criteria.

18.3.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.3.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

18.7. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥ 100 ppm to 3 significant figures.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

19. ►CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations ***Director***, Project Manager, ***Quality Control Director***, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique, or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. ►CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the ***group leader*** of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. ►WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by ***Eurofins*** Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. 2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998 (Committee approval 1997).

22.2. 2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 (Committee approval 1997).

22.3. 2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997/Edited 2011).

22.4. 2510 A. Conductivity, Introduction, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 (Committee approval 1997).

22.5. 2510 A. Conductivity, Introduction, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997/Edited 2011).

22.6. EPA Method 160.1: Residue, Filterable (Gravimetric, Dried at 180°C), Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.7. Total Dissolved Solids (TDS), EPA Method 160.1 (Gravimetric, Dried at 180°C, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, November 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Procedure Outline.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Projects.

24. ►MODIFICATIONS

24.1. The following modifications from SM 2540C. are noted:

Calscience SOP M713 Section	Reference Document SM 2540C Section	Summary of Modification
12.2.2.1	3d	The RPD control limit is modified.
14.15 - 14.16	3d	The filtrate evaporation procedure is modified.

24.2. The following modifications from EPA Method 160.1 are noted:

Calscience SOP M713 Section	Reference Document EPA 160.1 Section	Summary of Modification
14.4.3	7.3	The volume of aqueous sample filtered is modified.
14.15 - 14.16	7.5	The filtrate evaporation procedure is modified.
		EPA Region 9 requirements on contract required detection limit (CRDL), analytical balance check acceptance criteria, and mineral reference sample analyses are not applied.

25. ►REVISION HISTORY

Revision	Description	Author	Effective Date
2.7	Section 2: Update matrices. Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 22: Update references. Section 23: Add appendices. Section 24: Add Modification tables. Section 25: Add Revision History.	K. Burney	12/16/2013
2.8	Entire documents: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 19 and 20: Update responsibilities.	L. Hunt	03/23/2015

Appendix A

PROCEDURE OUTLINE

Eurofins Calscience, Inc.

SOP-M713, Revision 2.7

SM 2540 C PROCEDURE OUTLINE

Total Dissolved Solids (Filterable Residue, Gravimetric)

PROCEDURE

1) Determine conductivity of samples and record in TDS Logbook.
2) Prepare beakers (write ID #, heat in TDS oven 1 hour, cool, weigh).
3) Homogenize aqueous sample and measure 20mL in graduated cylinder.
4) Homogenize solid sample and weigh 3.0g into specimen container; add 20mL reagent water and sonicate 30 minutes.
5) Assemble vacuum filtration apparatus and insert filter in funnel.
6) Wet with reagent water to seat; if not pre-cleaned, wash 3x with 20mL reagent water.
7) Apply vacuum until all water gone; discard washings.
8) Insert clean 50mL graduated cylinder in the filtration flask.
9) Apply vacuum and decant sample onto filter without splashing.
10) Rinse filter 3x with ~ 10mL reagent water with complete drainage in between.
11) Continue to apply vacuum for 3 minutes or until all water gone.
12) Turn off pump; carefully remove graduated cylinder with tongs or forceps.
13) Pour filtrate into pre-weighed beaker.
14) Place beaker on hot plate at 80-100°C and dry until no visible water remains.
15) Dry residue in TDS oven for at least one hour; cool in desiccator.
16) Weigh beaker and record mass.
17) Repeat drying cycle until constant mass obtained.

Special requirements for DoD projects:

Must have MB, LCS and sample duplicate.

APPROVED BY: _____

DATE: _____

SOP-M713, Revision 2.7

SM 2540 C PROCEDURE OUTLINE

Total Dissolved Solids (Filterable Residue, Gravimetric)

REAGENTS

1) Reagent water, interferant free
2) Sand, washed, sea or standard Ottawa.
3) Sodium chloride, NaCl.

QC REQUIREMENT

MB/LCS/LCSD - per batch of 20 samples

Sample Duplicate - every 10 samples

APPROVED BY: _____

DATE: _____

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2540C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, Gravimetric) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. QUALITY CONTROL

3.1. Limit of Detection (LOD)

3.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

3.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

3.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.

3.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

3.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

3.1.2.3. If these criteria are not met, perform either one of the following tasks.

3.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

3.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

3.1.3. No samples shall be analyzed without a valid LOD.

3.2. Limit of Quantitation (LOQ)

3.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

3.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

3.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

3.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

3.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

3.2.2.2. LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.

3.3. Event Based Quality Control (LCS and MBs)

3.3.1. Laboratory Control Sample (LCS)

3.3.1.1. The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."

3.3.1.1.1. Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

3.3.1.2. The LCS shall be analyzed at a minimum frequency of one per preparation batch.

3.3.1.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.3.1.3. The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.

3.3.2. Method Blanks (MBs)

3.3.2.1. The method blank is used to assess the preparation batch for possible contamination during the preparation and processing

steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated.

3.3.2.1.1. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

3.3.2.2. The method blank shall be analyzed at a minimum of 1 per preparation batch.

3.3.2.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.3.2.3. The MB is considered to be contaminated if one of the following conditions is met.

3.3.2.3.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

3.3.2.4. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

3.3.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

3.4. Matrix Based Quality Control (Sample Duplicates)

3.4.1. Sample duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method.

3.4.1.1. The sample duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.

3.4.2. The frequency of the analysis of sample duplicates may be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the mandated test method.

3.4.3. Each preparation batch of samples must contain an associated sample duplicate using the same matrix collected for the specific DoD project.

3.4.3.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.4.4. The results from sample duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments..

3.4.5. Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.

3.4.5.1. For sample duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.

4. REFERENCES

4.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

Title : **SM 2540 D / EPA METHOD 160.2, TOTAL SUSPENDED SOLIDS (NON-FILTERABLE RESIDUE, GRAVIMETRIC)**

Document No. : SOP-M714
Revision No. : 1.5
Supersedes : 1.4

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PROPRIETARY INFORMATION STATEMENT

Revision 1.5 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 08/05/13
MANAGEMENT DATE

_____ 08-05-13
QA DEPARTMENT DATE

1. METHOD IDENTIFICATION

1.1. SM 2540 D / EPA Method 160.2, Total Suspended Solids (Non-Filterable Residue, Gravimetric).

2. APPLICABLE MATRICES

2.1. This method is applicable to drinking, surface and saline waters, domestic and industrial wastewaters.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Concentration (mg/L) in Sample	EQL (mg/L)
≥ 1.0 and < 1,000	1.0
≥ 1,000 and < 10,000	10
≥ 10,000 and < 100,000	100
≥ 100,000	1000

4. SCOPE AND APPLICATION

4.1. SM 2540 D / EPA Method 160.2 are used to determine the total suspended solids.

4.2. This method is restricted to use by or under the supervision of analysts experienced in the use of the equipment and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

4.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. A well-mixed sample is filtered through a weighed standard glass fiber filter, and the residue retained on the filter is dried to a constant weight at 103−105°C. The increase in weight of the filter represents the total suspended solids.

5.1.1. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume.

5.2. The filtrate from this method may be used for the determination of total dissolved solids (filterable residue).

5.3. An estimate of total suspended solids may be obtained by calculating the difference between total dissolved solids and total solids.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. ►Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client specific QAPP guidance overrides this directive to a lesser time period or the method specific SOP provides a different time period.*** An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

6.10. Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed

simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.15. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.22. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly

prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.23. Terms Specific to Solids Analysis

6.23.1. Total Dissolved Solids: The portion of total solids that passes through a filter of 2.0-µm (or smaller) nominal pore size under specified conditions.

6.23.2. Total Solids: Material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include total dissolved solids and total suspended solids.

6.23.3. Total Suspended Solids: The portion of total solids retained on a filter of 2.0-µm nominal pore size under specified conditions.

7. INTERFERENCES

7.1. Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling.

7.1.1. Mix small samples with a magnetic stirrer. Avoid using a magnetic stirrer if the samples contain magnetic particles.

7.1.2. If suspended solids are present, pipet with wide-bore pipets.

7.1.3. If part of a sample adheres to the sample container, document it in the logbook when evaluating and reporting results.

7.1.4. Exclude large, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not representative.

7.2. Some samples may dry with the formation of a crust that prevents water evaporating.

7.2.1. Limit sample to no more than 200 mg residue to prevent water-trapping crust.

7.3. Weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, gases from heat-induced chemical decomposition, and weight gains due to oxidation depend on the temperature and heating time at which the residue is dried.

7.3.1. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator to prevent moist air from entering.

7.3.2. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

7.4. Residue dried at 103–105°C may retain water of crystallization and some mechanically occluded water. Loss of carbon dioxide may convert bicarbonate to carbonate. Loss of organic matter by volatilization is usually very slight.

7.4.1. The removal of occluded water is marginal at this temperature; hence, attainment of constant weight may be very slow.

7.5. Residues high in oil or grease may yield questionable results because of the difficulty of drying to constant weight in a reasonable time.

7.5.1. Disperse visible floating oil and grease with a blender before withdrawing a sample aliquot for analysis.

7.6. Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

7.7. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material.

7.8. Prolonged filtration times resulting from filter clogging may produce high results due to increased colloidal materials captured on the clogged filter.

8. SAFETY

8.1. Watch glasses are heated in an oven and will be hot upon removal. Use tongs to handle the weighing dishes when removing from the oven.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Graduated cylinders, 100-mL, 500-mL, 1000-mL, or other capacity, glass, Class A.

9.2. Blender or homogenizer.

9.3. Magnetic stirrer.

9.4. Stir bars, Teflon coated.

9.5. Stir bar retriever, magnetic.

9.6. Transfer pipets, wide-bore, glass or plastic, disposable.

9.7. Vacuum filtration apparatus:

9.7.1. Vacuum apparatus.

9.7.2. Buchner funnel, 100-mm diameter, 320-mL capacity, porcelain with fixed perforated plate, capable of supporting a 90-mm diameter filter, CoorsTek Fixed Plate Buchner Funnel or equivalent.

9.7.3. Filtration flask, 1000-mL or other capacity, glass, with tubulation.

9.7.4. Filter paper, 1.5-µm effective pore size, 90-mm diameter, borosilicate glass microfiber, binder free, Whatman Grade 934-AH Glass Microfiber Filter or equivalent.

9.8. Watch glasses, 3½-in (90-mm) diameter or larger, concave shape with fire-polished edges.

9.9. Drying oven, thermostatically controlled, forced draft, capable of maintaining 104 ± 1°C.

9.10. Muffle furnace, capable of maintaining 550 ± 50°C.

9.11. Thermometer, calibrated, capable of monitoring temperatures at 104 ± 1°C.

9.12. Desiccator, containing indicating-type desiccant.

9.13. Forceps or tongs, stainless steel.

9.14. Gloves, heat resistant.

9.15. Wash bottle, 500-mL, 1000-mL, or other capacity, low density polyethylene (LDPE).

9.16. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.17. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.18. Aluminum foil.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, deionized.

10.1.2. Infusorial earth, white, calcined powder, Fisher I22-3, or equivalent.

10.1.3. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Laboratory Control Sample solution (LCS), 100ppm.

10.2.1.1. Prepare the LCS solution by weighing 0.4000 ± 0.0001g of infusorial earth on an analytical balance. Transfer the earth to a 4L volumetric flask and add reagent water to volume. Mix thoroughly and store in amber bottles.

10.2.2. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 1-L pre-cleaned high density polyethylene (HDPE) or clear glass containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.2. ►Samples should be maintained in a chilled state, ***0-6°C, not frozen***, post sample collection until received at the laboratory, ***where they are stored under refrigerated conditions***.

11.2.1. Aqueous samples shall be analyzed as soon as feasible to minimize microbiological decomposition of solids. The maximum holding time is within 7 days of sample collection.

11.3. Additional sample handling information can be found in the Sample Control SOPs.

12. QUALITY CONTROL

12.1. Event Based Quality Control (LCS/LCSDs and MBs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.1.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.1.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%.

12.1.3. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.

12.2. Matrix Based Quality Control (Sample Duplicates)

12.2.1. Matrix based quality control consists of QC samples processed using actual environmental samples. This consists of a sample duplicate.

12.2.1.1. A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples.

12.2.2. The acceptance criteria for duplicate analyte are as follows:

12.2.2.1. The RPD is ≤ 10%.

12.2.2.1.1. For EPA Region 9 requirement, the RPD is < 20%.

12.2.2.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

12.2.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

12.3. If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.4. Additional information regarding internal quality control check is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. ►Analytical Balance

13.1.1. Calibrate the analytical balance at ***2 mg***, 1 g, and 100 g using Class 2 weights ***as outlined in the current revision of SOP-T043.***

13.1.2. ***If control limits are not specified***, calibration shall be within ± ***0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits.*** If the values are not within these limits, recalibrate the balance

13.2. ►Top Loading Balance

13.2.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights ***as outlined in the current revision of SOP-T043***.

13.2.2. ***If control limits are not specified***, calibration shall be within ± 2% ***or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits.*** If the values are not within these limits, recalibrate the balance.

13.3. Thermometer

13.3.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

14. PROCEDURE

14.1. Watch Glass Preparation

14.1.1. Wash watch glass as outlined in the current revision of SOP-T014, and rinse thoroughly with deionized water.

14.1.2. Bake the freshly rinsed watch glass in an oven at 104°C ± 1°C for at least one hour. Remove the dried watch glass from oven and allow it to cool in a desiccator.

14.1.3. Store clean watch glass in a desiccator until needed.

14.1.4. Forceps or tongs shall be used for handling clean watch glass to prevent transfer of foreign deposits onto watch glass.

14.2. Filter Paper Preparation

14.2.1. Assemble a vacuum filtration apparatus with a clean filtration flask and Buchner funnel.

14.2.2. Using a fine point Sharpie, write an identification number on the edge of a filter paper.

14.2.2.1. Handle filter paper using clean forceps throughout the course of filter paper preparation.

14.2.2.2. Do not use fingers. Oils or other contaminants from fingers or gloves may change the mass of the filter paper.

14.2.3. Place the filter paper in the Buchner funnel and apply vacuum.

14.2.4. Using wash bottle, rinse the filter paper with three successive 20-mL portions of reagent water.

14.2.5. Continue to apply vacuum until all traces of water have been removed. Turn the vacuum pump off and discard the washings.

14.2.6. Remove the filter paper from the funnel and place on a clean aluminum foil covered shelf in an oven.

14.2.7. Dry the filter paper in the oven at 103−105°C for one hour.

14.2.7.1. If volatile solids are to be measured, heat the filter paper in a muffle furnace at 550°C ± 50°C for 15 minutes instead.

14.2.8. Remove the filter paper from the oven, transfer to a desiccator, and allow to cool.

14.2.9. When cool to ambient temperature, and immediately prior to sample preparation, weigh the filter paper on a calibrated analytical balance. Record the filter paper identification number and the mass to the nearest 0.1 mg (or 0.0001 g).

14.2.9.1. Shut all access doors on the balance and tare. Open a single access door, remove a single filter from the desiccator, and place on the balance pan. Shut the access door and allow the digital readout to stabilize before recording the mass.

14.2.9.2. Repeat the drying cycle (Section 14.2.7. to Section 14.2.8.) until a constant mass is obtained. The mass change shall be less than 4% of the previous mass or 0.5 mg, whichever is less.

14.2.9.3. Place the filter paper on a clean watch glass for immediate use, or store it in the desiccator.

14.3. Aqueous Sample Preparation

14.3.1. Allow an aqueous sample to reach ambient temperature.

14.3.2. Homogenize the aqueous sample by shaking the sample thoroughly. Invert the sample container at least three times while shaking.

14.3.2.1. Sample may be homogenized by stirring with a magnetic stirrer at a speed to shear large particles.

14.3.3. Quickly measure 100 ± 5 mL of the homogenized aqueous sample into a Class A graduated cylinder. Excess volume may be removed with a disposable transfer pipet. Record the volume to the nearest 1 mL or 3 significant figures.

14.3.3.1. For MB, measure exactly 1000 mL of clean reagent water.

14.3.3.2. For LCS/LCSD, measure exactly 100mL of the 100ppm standard solution.

14.3.3.3. The sample volume shall yield between 2.5-mg and 200-mg dried residue. If the volume filtered fails to meet the minimum yield, increase the sample volume up to 1000 mL. If complete filtration takes more than 10 minutes, increase the filter diameter or decrease the sample volume.

14.3.4. Proceed to Section 14.4. for filtration procedure.

14.4. Assemble a vacuum filtration apparatus with a clean filtration flask and Buchner funnel.

14.5. Place a pre-weighed filter paper in the Buchner funnel and apply vacuum.

14.5.1. Handle filter paper using clean forceps throughout the course of sample preparation and analysis.

14.6. Using wash bottle, wet the filter paper with a small volume of reagent water to seat it on the funnel.

14.6.1. If the sample aliquot is not ready to be filtered immediately, turn the vacuum pump off to prevent the filter paper from becoming dry and possibly unseating itself from the funnel.

14.7. Apply vacuum and carefully decant the measured sample onto and through the filter paper without splashing. Continue filtration with the vacuum operating.

14.8. Using wash bottle, rinse the graduated cylinder, filter paper, residue, and funnel wall thoroughly with three successive 20-mL portions of reagent water. Allow complete drainage between washings, and continue to apply vacuum for about 3 minutes after filtration is complete or until all visible water is removed.

14.8.1. Sample with high dissolved solids or high salt content may require additional washings.

14.9. Turn the vacuum pump off. Carefully remove the filter paper from the funnel with forceps at the edge of the filter paper and place on a clean watch glass.

14.9.1. Do not touch the residue or invert the filter paper.

14.10. Transfer the watch glass and filter paper to an oven designated for the analysis.

14.10.1. Check the oven temperature prior to placing the watch glass and filter paper inside. The acceptable temperature range is 103−105°C.

14.10.2. Check the temperature log and/or the actual thermometer to be sure the oven is in proper working condition.

14.11. Dry the residue and the filter paper in the oven at 103−105°C for at least one hour.

14.12. Remove the watch glass and filter paper from the oven using clean tongs or forceps, transfer to a desiccator and allow to cool.

14.13. When cool to ambient temperature, weigh the filter paper including the dried residue on a calibrated analytical balance. Record the mass to the nearest 0.1 mg (or 0.0001 g).

14.13.1. Repeat the drying cycle (Section 14.11. to Section 14.12.) until a constant mass is obtained. The mass change shall be less than 4% of the previous mass or 0.5 mg, whichever is less.

14.14. Samples are filtered one at a time in the following or other logical order:

1) Method Blank (MB)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Samples (up to 20 per batch, excluding QA samples)
5) Sample Duplicate

14.14.1. Item 1: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.14.1.1. For aqueous samples, the MB consists of clean reagent water.

14.14.1.2. One MB is required every day preparatory procedures (i.e., filtrations, dryings, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.14.2. Item 2: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.14.2.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water

14.14.2.2. One LCS is required every day sample preparations are performed for every batch of 20 samples or portion thereof, whichever is more frequent.

14.14.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is

expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.

14.14.4. Item 4: Up to 20 samples (excluding method blanks) per batch.

14.14.5. Item 5: The sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.

14.14.5.1. The purpose of the sample duplicate is to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.

14.14.5.2. One sample duplicate is required for every batch of 10 samples per matrix or portion thereof processed concurrently.

14.14.5.2.1. For EPA Region 9 requirement, one sample duplicate is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.15. Thoroughly document all aspects of the preparatory procedures in the Gravimetric Logbook for Total Suspended Solids. This logbook includes, but is not limited to:

14.15.1. Preparation and analysis dates.

14.15.2. Sample volume.

14.15.3. Filter paper and dried residue masses.

14.15.4. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

14.16. Data Interpretation

14.16.1. Determine the total suspended solids of a sample from the sample volume, and the filter paper masses before and after sample filtration. The formula for calculating the concentration of total suspended solids is listed in Section 15.2.

15. CALCULATION

15.1. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).

C_1 = concentration of total suspended solids in measurement 1.
C_2 = concentration of total suspended solids in measurement 2.

Note: Concentrations must be in equivalent units.

15.2. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_{TSS} = \frac{(M_f - M_i) \times 1000}{V_A}$$

where: C_{TSS} = concentration of total suspended solids (TSS) in mg/L.
M_f = mass of filter paper and oven-dried residue in mg.
M_i = mass of filter paper in mg.
V_A = volume of aqueous sample filtered in mL.

15.3. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

15.4. Report TSS concentrations which are < 100 ppm to 2 significant figures, and TSS concentrations which are ≥ 100 ppm to 3 significant figures.

15.5. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits.

18.2.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.3. The acceptance criteria for duplicate analyte are predetermined. The RPD is ≤ 10%.

18.3.1. For EPA Region 9 requirement, refer to Section 12.2.2.1.1. for acceptance criteria.

18.3.2. When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.3.3. If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. All concentrations shall be reported in mg/L (ppm) for aqueous samples.

18.7. Report TSS concentrations which are < 100 mg/L to 2 significant figures, and TSS concentrations which are ≥ 100 mg/L to 3 significant figures.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *2540 D. Total Suspended Solids Dried at 103–105°C*, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998 (Committee approval 1997).

22.2. *2540 D. Total Suspended Solids Dried at 103–105°C*, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005 (Committee approval 1997).

22.3. *2540 D. Total Suspended Solids Dried at 103–105°C,* Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012 (Committee approval 1997 / Edited 2011).

22.4. EPA Method 160.2: Residue, Non-Filterable (Gravimetric, Dried at 103–105°C), Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.5. Total Suspended Solids (TSS), EPA Method 160.2 (Gravimetric, Dried at 103–105°C, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, November 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Projects.

23.2. ***►Appendix B: Appendix J to Part 50 – Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere.***

24. MODIFICATIONS

24.1. The following modifications from SM 2540 D. are noted:

Calscience SOP M714 Section	Reference Document SM 2540 D Section	Summary of Modification
12.2.2.1	3c	The RPD control limit is modified.
14.8	3c	The volume of reagent water used to rinse the filter paper and residue is modified.

24.2. The following modifications from EPA Method 160.2 are noted:

Calscience SOP M714 Section	Reference Document EPA 160.2 Section	Summary of Modification
9.7.4	6.1	The filter paper diameter is modified.
14.3.3.2	7.2	The minimum residue yield is modified.
		EPA Region 9 requirements on contract required detection limit (CRDL), analytical balance check acceptance criteria, and mineral reference sample analyses are not applied.

25. REVISION HISTORY

Revision	Description	Author	Effective Date
1.4	Section 6: Update definitions. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample container and storage. Section 12: Update QC requirements. Section 13: Update calibration. Section 14: Update procedure. Section 18: Update data assessment. Section 22: Update references. Section 23: Add appendix. Section 24: Add Modification tables. Section 25: Add Revision History.	K. Burney	02/18/2013
1.5	Section 11: Update sample storage. Section 13: Update calibration. Section 23: Add appendix B. Section 25: Update Revision History.	K. Burney	

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. SM 2540 D / EPA Method 160.2, Total Suspended Solids (Non-Filterable Residue, Gravimetric) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. QUALITY CONTROL

3.1. Limit of Detection (LOD)

3.1.1. LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

3.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

3.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.

3.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).

3.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

3.1.2.3. If these criteria are not met, perform either one of the following tasks.

3.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

3.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

3.1.3. No samples shall be analyzed without a valid LOD.

3.2. Limit of Quantitation (LOQ)

3.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

3.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

3.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

3.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

3.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

3.2.2.2. LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.

3.3. Event Based Quality Control (LCS and MBs)

3.3.1. Laboratory Control Sample (LCS)

3.3.1.1. The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."

3.3.1.1.1. Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

3.3.1.2. The LCS shall be analyzed at a minimum frequency of one per preparation batch.

3.3.1.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.3.1.3. The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.

3.3.2. Method Blanks (MBs)

3.3.2.1. The method blank is used to assess the preparation batch for possible contamination during the preparation and processing

steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated.

3.3.2.1.1. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

3.3.2.2. The method blank shall be analyzed at a minimum of 1 per preparation batch.

3.3.2.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.3.2.3. The MB is considered to be contaminated if one of the following conditions is met.

3.3.2.3.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

3.3.2.3.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

3.3.2.4. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

3.3.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

3.4. Matrix Based Quality Control (Sample Duplicates)

3.4.1. Sample duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method.

3.4.1.1. The sample duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.

3.4.2. The frequency of the analysis of sample duplicates may be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the mandated test method.

3.4.3. Each preparation batch of samples must contain an associated sample duplicate using the same matrix collected for the specific DoD project.

3.4.3.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

3.4.4. The results from sample duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments..

3.4.5. Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.

3.4.5.1. For sample duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.

4. REFERENCES

4.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

►***Appendix B***

APPENDIX J TO PART 50 – REFERENCE METHOD FOR THE DETERMINATION OF PARTICULATE MATTER AS PM_{10} IN THE ATMOSPHERE

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ***Appendix J to Part 50 – Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere.***

2. APPLICABLE MATRICES

2.1. ***This method is applicable to air.***

3. DETECTION LIMITS

3.1. ***The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading beyond which the sampler no longer maintains the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM_{10} mass concentrations of at least 300 µg/ std m3 while maintaining the operating flow rate within the specified limits.***

4. SCOPE AND APPLICATION

4.1. ***This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM_{10}) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in § 50.6 of 40 CFR chapter 1. The measurement process is nondestructive, and the PM_{10} sample can be subjected to subsequent physical or chemical analyses.***

4.2. ***This method is restricted to use by or under the supervision of analysts experienced in the use of the equipment and apparatus required to execute the analysis and skilled in the interpretation of the outputs.***

4.2.1. ***Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.***

5. METHOD SUMMARY

5.1. ***An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range. Each size fraction in the***

PM_{10} size range is then collected on a separate filter over the specified sampling period.

5.2. ***Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, corrected to EPA reference conditions (25 C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the volume of air sampled, and is expressed in micrograms per standard cubic meter (µg/std m^3).***

6. EQUIPMENT AND SUPPLIES

6.1. ***Desiccator, containing indicating-type desiccant.***

6.2. ***Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.***

6.3. ***Specimen containers, 4.5-oz (120-mL), plastic, disposable.***

7. PROCEDURE

7.1. ***Immediately upon receipt of the sampled PM_{10} filters, place them in a desiccator for a minimum of 24 hours.***

7.2. ***After the desiccation period, remove one filter at a time and carefully roll it into a cylinder small enough to fit into a specimen cup.***

7.2.1. ***Be sure to wear clean gloves when handling filters – do not touch them with bare hands.***

7.3. ***Place a specimen cup in the analytical balance and tare the balance.***

7.4. ***Place the rolled filter into the cup on the balance and record the mass in the logbook.***

7.5. ***Repeat the weighing process for each sample in the batch, recording all pertinent information in the logbook.***

8. CALCULATIONS

8.1. ***Using the air volumes and initial weights provided by the client, calculate the PM_{10} concentration as follows:***

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

Where

PM_{10}	=	mass concentration of PM_{10}, µg/std m^3
W_f	=	final weight of filter after collecting PM_{10} particles, in g
W_i	=	initial weight of filter before collecting PM_{10} particles, in g
10^6	=	conversion of g to µg
V_{std}	=	total air sampled in standard volume units, std m^3

9. *REFERENCES*

9.1. ***Code of Federal Regulations, Title 40, Chapter 1, Appendix J to Part 50 – Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere, USEPA, 2011 edition.***

Title : **SM 4500-NH_3 B/C / EPA METHOD 350.2, AMMONIA AS NITROGEN (DISTILLATION, TITRIMETRIC METHOD)**

Document No. : SOP-M717
Revision No. : 1.3
Supersedes : 1.2

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PROPRIETARY INFORMATION STATEMENT

Revision 1.3 changes, other than NELAC formatting, are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY:

	MANAGEMENT	08/13/08 **DATE**
	QA DEPARTMENT	0808-08 **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. ►SM 4500-NH_3 B/C / EPA Method 350.2, Ammonia as Nitrogen (Distillation, Titrimetric Method).

2. APPLICABLE MATRICES

2.1. ►This method is applicable to drinking, surface and saline waters, domestic and industrial wastes. ***It is also applicable to solid and other non-aqueous wastes as a modified method.***

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are 0.10 mg/L for aqueous samples, 5.00 mg/kg for soil and solid samples, and 0.20 mg/kg for marine sediment samples.

3.2. The EQLs will be proportionally higher for samples which require dilution or reduced sample size.

4. ►SCOPE AND APPLICATION

4.1. ***SM 4500-NH_3 B/C / EPA Method 350.2 is used to determine the concentrations of ammonia-nitrogen exclusive of total Kjeldahl nitrogen in various matrices.***

4.1.1. ***The method is suitable for ammonia-nitrogen in the concentration range of 5 to 25 mg/L.***

4.2. ***This method is restricted to use by or under the supervision of analysts experienced in the use of the instruments and apparatus required to execute the analysis and skilled in the interpretation of the outputs.***

4.2.1. ***Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.***

5. METHOD SUMMARY

5.1. The sample is buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds. The buffered sample is then distilled into a solution of boric acid. The ammonia in the distillate is determined titrimetrically with standard H_2SO_4 and a mixed indicator.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.10. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.11. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.12. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.13. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.14. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.15. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.16. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.17. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.18. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.19. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.20. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. ►INTERFERENCES

7.1. ***Urea and cyanates hydrolyze on distillation at pH of 9.5. Hydrolysis amounts to about 7% for urea and about 5% for cyanates.***

7.2. ***Volatile alkaline compounds such as hydrazine and amines influence titrimetric results.***

7.3. ***Residual chlorine reacts with ammonia. Remove residual chlorine by sample pretreatment prior to distillation.***

7.3.1. ***If a sample is likely to contain residual chlorine, treat with a dechlorinating reagent (such as sodium thiosulfate) upon collection by adding 1 mL of dechlorinating reagent per 1-mg/L residual chlorine in the sample.***

8. SAFETY

8.1. ►Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current ***version of Calscience's Health, Safety, and Respiratory Protection Manual***. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDS) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. ***Buret, borosilicate glass, 50-mL.***

9.2. ***Specimen containers, 8-oz (250-mL), with lids, plastic, disposable.***

9.3. pH meter, ***Fisher Scientific Accumet Basic AB15 pH meter equipped with ATC probe or equivalent***.

9.4. ***Combination pH/reference electrode, gel-filled type.***

9.5. ***pH indicator paper, narrow range. pH range should include the desired pH.***

9.6. Potassium iodide-starch test strips, ***white color paper***.

9.6.1. ***The potassium iodide-starch test paper turns blue to deep purple in the presence of chlorine, iodine, peroxide, and ozone.***

9.7. Graduated cylinders, 50-mL and 500-mL, glass, Class A.

9.8. ***Pipetter, 0.5–5.0-mL, adjustable, with disposable tip.***

9.9. ***Pipets, transfer, plastic and glass, disposable.***

9.10. Volumetric flasks, 500-mL and 1-L, glass, Class A.

9.11. ***Balance, analytical, capable of weighing to the nearest 0.1 mg.***

9.12. ***Balance, top loading, capable of weighing to the nearest 0.01 g.***

9.13. Distillation apparatus:

9.13.1. ***Distillation (boiling) flask, 1-L, borosilicate glass.***

9.13.2. ***Graham condenser, borosilicate glass.***

9.13.3. ***Delivery tube, Teflon.***

9.13.4. ***Heating mantle, rheostat controlled.***

9.13.5. Boiling chips, ***Teflon***.

9.14. ***Dry weight determination apparatus:***

9.14.1. ***Refer to SOP-M700 for equipment and supplies.***

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, ***ammonia*** free, ***deionized or nano-pure***.

10.1.2. ***Sand, washed, sea or standard Ottawa.***

10.1.3. ***Sodium thiosulfate, $Na_2S_2O_3$, pentahydrate or anhydrous, granular, reagent grade or equivalent.***

10.1.4. ***Dechlorinating reagent***, sodium thiosulfate.

10.1.4.1. Prepare the dechlorinating reagent by dissolving ***1.75 g*** of $Na_2S_2O_3 \cdot 5H_2O$ ***(or 1.11 g of anhydrous $Na_2S_2O_3$)*** in reagent water and dilute to ***500 mL*** with additional reagent water.

10.1.4.2. The dechlorinating reagent must be prepared fresh weekly.

10.1.5. ***Sodium hydroxide, NaOH, 0.1-N.***

10.1.5.1. ***Prepare the solution by dissolving 4.0 g of NaOH (reagent grade or equivalent) in reagent water, cool and dilute to 1 L.***

10.1.6. Sodium hydroxide, NaOH, 1-N.

10.1.6.1. ***Prepare the solution by dissolving 20.0 g of NaOH (reagent grade or equivalent) in reagent water, cool and dilute to 500 mL.***

10.1.7. ***Sodium hydroxide, NaOH, 6-N.***

10.1.7.1. ***Prepare the solution by dissolving 240 g of NaOH (reagent grade or equivalent) in reagent water, cool and dilute to 1 L.***

10.1.8. ***Sodium tetraborate, $Na_2B_4O_7$, decahydrate or anhydrous, reagent grade or equivalent.***

10.1.9. Buffer solution, borate.

10.1.9.1. ***Prepare the 0.025-M sodium tetraborate solution by dissolving 4.75 g of $Na_2B_4O_7 \cdot 10H_2O$ (or 2.51 g of anhydrous $Na_2B_4O_7$) in 500 mL of reagent water.***

10.1.9.2. ***Prepare the borate buffer solution by adding 88 mL of 0.1-N NaOH solution to the 0.025-M sodium tetraborate solution and dilute to 1 L with reagent water.***

10.1.10. ***Boric acid, H_3BO_3, crystalline, reagent grade or equivalent.***

10.1.11. Absorbent solution, boric acid, ***2% (w/v)***.

10.1.11.1. Prepare the absorbent solution by dissolving 20.0 g of H_3BO_3 in reagent water and dilute to 1 L with additional reagent water.

10.1.12. ***Ethyl alcohol (ethanol), C_2H_5OH, 95% (v/v), reagent grade or equivalent.***

10.1.13. ***Methyl red, $C_{15}H_{14}N_3O_2Na$, reagent grade or equivalent.***

10.1.14. ***Methylene blue, $C_{16}H_{18}ClN_3S$, reagent grade or equivalent.***

10.1.15. Mixed indicator solution.

10.1.15.1. ***Prepare the mixed indicator solution by dissolving 200 mg of methyl red and 100 mg of methylene blue in 150 mL of ethyl alcohol.***

10.1.15.2. The mixed indicator solution must be prepared fresh monthly.

10.1.16. Indicating boric acid solution.

10.1.16.1. Prepare boric acid solution by dissolving 20.0 g of H_3BO_3 in reagent water.

10.1.16.2. Add 10 mL of mixed indicator solution to boric acid solution, and dilute to 1 L with reagent water.

10.1.16.3. The indicating boric acid solution must be prepared fresh monthly.

10.1.17. ***Sodium carbonate, Na_2CO_3, anhydrous, reagent grade or equivalent.***

10.1.17.1. ***Dry 3–5 g of Na_2CO_3 at 140°C for 24 hours and cooled in a desiccator.***

10.1.18. ***Sulfuric acid, H_2SO_4, 1:1 (v/v), commercially prepared, reagent grade or equivalent.***

10.1.19. ***Sulfuric acid, H_2SO_4, 1-N, commercially prepared, reagent grade or equivalent.***

10.1.20. ***All reagents must be inspected and documented in the Solvent/Standard Verification Logbook prior to use.***

10.2. Standards

10.2.1. Standard sulfuric acid titrant, H_2SO_4, 0.02-N ***(1-mL = 0.280-mg NH_3-N), commercially prepared, NIST traceable, containing H_2SO_4 and reagent water, Fisher Scientific Catalog Number SA226-4 or equivalent.***

10.2.2. ***Sodium carbonate, Na_2CO_3, approximately 0.02-N.***

10.2.2.1. ***Prepare the solution by dissolving 0.530 g of anhydrous Na_2CO_3 in reagent water and dilute to 500 mL with additional reagent water.***

10.2.2.2. ***Do not keep the solution for more than one week.***

10.2.3. ***All stock standards must be inspected and documented in the Solvent/Standard Verification Logbook prior to use.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. ***Aqueous samples should be collected in 1-L pre-cleaned amber glass containers with Teflon-lined closures.***

11.1.1. Aqueous samples shall be preserved with 1:1 H_2SO_4 solution to pH < 2.

11.2. ***Soil samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.***

11.3. ***Samples should be maintained in a chill state (≤4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).***

11.4. Upon receipt, the samples are stored in a ***0–6°C*** cooler.

11.4.1. ***Aqueous samples with acid preservation (pH < 2) must be distilled and analyzed within 28 days of sample collection.***

11.4.2. ***Aqueous samples without acid preservation (pH ≥2) must be distilled and analyzed within 24 hours of sample collection.***

11.4.3. ***Non-aqueous samples must be distilled and analyzed within 28 days of collection.***

11.5. Additional sample handling information can be found in the Sample Control SOPs.

12. ►QUALITY CONTROL

12.1. ***Event Based Quality Control (MBs)***

12.1.1. ***Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB).***

12.1.2. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.1.2.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.1.2.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the

effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-analyzed.

12.1.3. A method blank ***consisting of reagent water*** should be analyzed for every batch of 20 samples ***or portion thereof. The method blank shall be carried through the entire analytical process***.

12.2. ***Matrix Based Quality Control (Sample Duplicates)***

12.2.1. ***Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a sample duplicate.***

12.2.2. ***The acceptance criteria for sample duplicates are as follows:***

12.2.2.1. ***The RPD is ≤25%.***

12.2.2.2. When the RPD of the sample duplicate is at or within the established acceptance limit, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. If the RPD of the sample duplicate is not within the established acceptance limits, the analytical system performance shall be suspect.

12.2.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

12.2.4. A sample duplicate should be analyzed for every batch of 20 samples ***or portion thereof. The sample in combination with the sample duplicate can be used to assess the precision of the analytical measurements. The measurement is expressed as the relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.***

12.3. ***If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-analyzed.***

12.4. Additional information regarding internal quality control check is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 10% at 2 mg (± 0.2 mg), or within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Top Loading Balance

13.2.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.2.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.3. Pipetter

13.3.1. Calibrate the pipetter according to the procedure outlined in the pipetter calibration logbook.

13.4. pH Meter

13.4.1. Calibrate the pH meter daily prior to sample analysis at pH of 4.00, 7.00, and 10.00 using fresh buffer solutions and according to the instrument manufacturer's recommended procedures.

13.4.2. Verify the calibration with fresh second source buffer standard. The second source standard shall not differ from its expected value by more than 0.05 pH units. If this criterion is not met, recheck calibration or effect corrective action.

13.4.3. The theoretical slope shall be within 90−105% for analysis to proceed. If this criterion is not met, determine the cause of the problem, effect corrective action, and recalibrate, if necessary.

13.5. Titrant Standardization

13.5.1. Transfer 50 mL of 0.02-N Na_2CO_3 solution into a beaker or specimen container.

13.5.2. Titrate potentiometrically to pH 4.5 by adding 0.02-N standard H_2SO_4 titrant.

13.5.3. Calculate the normality of titrant. The formula for calculating normality is listed in Section 15.1.

14. ►PROCEDURE

14.1. ***Distillation Equipment Preparation***

14.1.1. ***Assemble the distillation apparatus.***

14.1.2. Add 500 mL of reagent water and 20 mL of borate buffer solution into a clean distillation disk.

14.1.3. Adjust the pH of the solution in the distillation flask to 9.5 with 6-N NaOH solution.

14.1.4. Add a few boiling chips into the distillation flask, and steam out the distillation apparatus until distillate shows no traces of ammonia.

14.1.5. Leave the distillation apparatus assembled after steaming out without disconnecting any component to minimize contamination.

14.2. ***Aqueous Sample Preparation for SM 4500-NH_3 B/C***

14.2.1. Verify the presence of residual chlorine by ***transferring a few drops of an aqueous sample onto*** a potassium iodide-starch test strip. ***A blue to deep purple color indicates the presence of residual chlorine.***

14.2.1.1. ***If residual chlorine is present, add 0.5 mL of dechlorinating reagent, and then verify the presence of residual chlorine with a fresh potassium iodide-starch test strip. Repeat the procedure until residual chlorine is completely removed.***

14.2.2. Measure 500 mL of the ***dechlorinated*** aqueous sample or 500 mL of the diluted sample into a clean distillation flask. ***Record the volume of the sample used to the nearest 1 mL.***

14.2.2.1. ***For MB, measure 500 mL of clean reagent water.***

14.2.3. Adjust the pH to 7.0 with 1-N NaOH or 1-N H_2SO_4 solution ***if the sample was acid preserved***.

14.2.4. Add 25 mL of borate buffer solution into the sample, and adjust the pH to 9.5 with 6-N NaOH solution.

14.2.5. ***Add a few boiling chips into the distillation flask.***

14.2.6. Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.

14.2.7. Use a ***specimen container*** containing 50 mL of indicating boric acid solution ***(Section 10.1.16.)*** to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the indicating boric acid solution.

14.2.8. Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.

14.2.8.1. Continue distillation during the last minute or two, but lower the ***specimen container*** such that the end of the delivery tube is free of contact with the liquid to cleanse the condenser and the delivery tube.

14.2.9. ***If the solution color appears to be purple, report the concentration of NH_3-N as non-detected (ND). If the solution color appears to be green, proceed to Section 14.5.***

14.3. ***Non-Aqueous Sample Preparation for SM 4500-NH_3 B/C***

14.3.1. ***If sample results are to be reported on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.***

14.3.1.1. ***Refer to SOP-M700 for determination of solids content.***

14.3.2. Measure ***10.0 g*** of a solid sample ***or 250 g of a marine sediment sample*** into a clean distillation flask. ***Record the mass of the solid sample used to the nearest 0.1 g or the mass of the marine sediment sample used to the nearest 1 g.***

14.3.2.1. ***For solid MB, measure 10.0 g of washed sea sand.***

14.3.2.2. ***For marine sediment MB, measure 250 g of washed sea sand.***

14.3.3. Add 500 mL of reagent water into the sample.

14.3.4. ***Add 25 mL of borate buffer solution into the sample, and adjust the pH to 9.5 with 6-N NaOH solution.***

14.3.5. ***Add a few boiling chips into the distillation flask.***

14.3.6. ***Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.***

14.3.7. ***Use a specimen container containing 50 mL of indicating boric acid solution (Section 10.1.16.) to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the indicating boric acid solution.***

14.3.8. ***Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.***

14.3.8.1. ***Continue distillation during the last minute or two, but lower the specimen container such that the end of the delivery tube is free of contact with the liquid to cleanse the condenser and the delivery tube.***

14.3.9. ***If the solution color appears to be purple, report the concentration of NH_3-N as non-detected (ND). If the solution color appears to be green, proceed to Section 14.5.***

14.4. ***Aqueous Sample Preparation for EPA Method 350.2***

14.4.1. ***Verify the presence of residual chlorine by transferring a few drops of an aqueous sample onto a potassium iodide-starch test strip. A blue to deep purple color indicates the presence of residual chlorine.***

14.4.1.1. ***If residual chlorine is present, add 0.5 mL of dechlorinating reagent, and then verify the presence of residual chlorine with a fresh potassium iodide-starch test strip. Repeat the procedure until residual chlorine is completely removed.***

14.4.2. Measure 400 mL of the ***dechlorinated*** aqueous sample ***or 400 mL of the diluted sample*** into a clean distillation flask. ***Record the volume of sample used to the nearest 1 mL.***

14.4.2.1. ***For MB, measure 400 mL of clean reagent water.***

14.4.3. ***Adjust the pH to 9.5 with 1-N NaOH.***

14.4.4. Add 25 mL of borate buffer solution into the sample.

14.4.5. ***Add a few boiling chips into the distillation flask.***

14.4.6. Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.

14.4.7. Use a ***specimen container*** containing 50 mL of ***absorbent solution (Section 10.1.11.)*** to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the ***absorbent solution***.

14.4.8. Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.

14.4.9. ***Proceed to Section 14.6.***

14.5. ***Sample Analysis for SM 4500-NH_3 B/C***

14.5.1. Titrate by adding 0.02-N standard H_2SO_4 titrant until a pale lavender color is displayed.

14.5.2. Record the volume of standard H_2SO_4 titrant used ***to the nearest 0.01 mL***.

14.6. ***Sample Analysis for EPA Method 350.2***

14.6.1. ***Add 3 drops of mixed indicator solution (Section 10.1.15.) to the distillate.***

14.6.1.1. ***If the solution color appears to be purple, report the concentration of NH_3-N as non-detected (ND). If the solution color appears to be green, proceed to Section 14.6.2.***

14.6.2. ***Titrate by adding 0.02-N standard H_2SO_4 titrant until a pale lavender color is displayed.***

14.6.3. ***Record the volume of standard H_2SO_4 titrant used to the nearest 0.01 mL.***

14.7. ***Data Interpretation***

14.7.1. ***Determine the concentration of ammonia-nitrogen of an aqueous sample from the volume of standard H_2SO_4 titrant used and the volume of sample used. The formula for calculating the concentration is listed in Section 15.2.***

14.7.1.1. ***Each 1 mL of 0.02-N standard H_2SO_4 titrant is equivalent to 280 mg/L of NH3-N in an aqueous sample.***

14.7.2. ***Determine the concentration of ammonia-nitrogen of a non-aqueous sample from the volume of standard H_2SO_4 titrant used and the mass of sample used. The formula for calculating the concentration is listed in Section 15.3.***

14.7.2.1. ***Each 1 mL of 0.02-N standard H_2SO_4 titrant is equivalent to 280 mg/kg of NH3-N in a non-aqueous sample.***

14.7.3. ***If the volume of standard H_2SO_4 titrant used exceeds 50 mL, dilute the aqueous sample or reduce the non-aqueous sample size, redistilled, and reanalyzed.***

15. ►CALCULATIONS

15.1. ***The normality of standard H_2SO_4 titrant is calculated as follows:***

$$N_{H2SO4} = \frac{N_{Na2CO3} \times V_{Na2CO3}}{V_{H2SO4}}$$

where: N_{H2SO4} = ***normality of standard H_2SO_4 titrant.***
N_{Na2CO3} = ***normality of sodium carbonate solution.***
V_{Na2CO3} = ***volume of sodium carbonate solution used in mL.***
V_{H2SO4} = ***volume of standard H_2SO_4 titrant used in mL.***

15.2. ***The target analyte concentration for an aqueous sample is calculated as follows:***

$$C_A = \frac{V_{H2SO4} \times 280 \times D}{V_A}$$

where: C_A = ***concentration of target analyte in aqueous sample in mg/L of NH_3-N.***
V_{H2SO4} = ***volume of standard H_2SO_4 in mL.***
V_A = ***volume of aqueous sample used in mL.***
D = ***dilution factor, if the sample was diluted prior to distillation. If no dilution was made, D = 1.***

15.3. ***The target analyte concentration for a non-aqueous sample is calculated as follows:***

$$C_S = \frac{V_{H2SO4} \times 280}{W_S \times W_p}$$

where: C_S = ***concentration of target analyte in non-aqueous sample in mg/kg of NH_3-N.***
V_{H2SO4} = ***volume of standard H_2SO_4 in mL.***
W_S = ***mass of non-aqueous sample used in g.***
W_p = ***percent dry weight (wet-based solids content). If no dry weight determination was made, W_p = 100%.***

15.4. ***The dilution factor is calculated as follows:***

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample after dilution in mL.
V_i = volume of sample before dilution in mL.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of ammonia as nitrogen in measurement 1.
C_2 = concentration of ammonia as nitrogen in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. ***All concentrations shall be reported in mg/L (ppm) of NH_3-N for aqueous samples, and mg/kg (ppm) of NH_3-N for soil and solid waste samples.***

15.7. ***The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.***

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. The acceptance criteria for the RPD of the sample duplicate is $\leq$25%.

18.2.1. When the RPD of the sample duplicate is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.2.2. If the RPD of the sample duplicate is not within the established acceptance limits, the analytical system performance shall be suspect.

18.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.

18.4. Additional information regarding internal quality control checks is provided in SOP-T020.

18.5. All concentrations shall be reported in mg/L (ppm) of NH_3-N for aqueous samples, and mg/kg (ppm) of NH_3-N for soil and solid waste samples.

18.6. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ►REFERENCES

22.1. ***4500-NH_3 B. Nitrogen (Ammonia), Preliminary Distillation Step, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.***

22.2. ***4500-NH_3 B. Nitrogen (Ammonia), Preliminary Distillation Step, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.***

22.3. *4500-NH_3 E. Nitrogen (Ammonia), Titrimetric Method*, Standard Methods for the Examination of Water and Wastewater, ***20th*** Edition, ***1998***.

22.4. ***4500-NH_3 E. Nitrogen (Ammonia), Titrimetric Method, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.***

22.5. *EPA Method 350.2: Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric Distillation Procedure)*, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Internal Quality Control Criteria.

23.2. Appendix B: General Inorganic Raw Data Form – MBDUP.

Appendix A

INTERNAL QUALITY CONTROL CRITERIA

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. SM 4500-NH_3 B/C / EPA Method 350.2, Ammonia as Nitrogen (Distillation, Titrimetric Method) – Internal Quality Control Criteria.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein are for internal use only to monitor distillation setup.

3. DEFINITIONS

3.1. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

3.2. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

4. EQUIPMENT AND SUPPLIES

4.1. Drying oven, capable of maintaining 104 ± 1°C.

4.2. Watch glass.

4.3. Desiccator.

4.4. Forceps or tongs, stainless steel.

5. REAGENTS AND STANDARDS

5.1. Reagents

5.1.1. Ammonium chloride, NH_4Cl, anhydrous, certified, reagent grade or equivalent.

5.1.1.1. Dry 4−5 g of NH_4Cl at 103−105°C for 24 hours and cooled in a desiccator.

5.1.2. The reagent must be inspected and documented in the Solvent/Standard Verification Logbook prior to use.

5.2. Standards

5.2.1. Spike standard solution containing 1000 mg/L of NH_3-N in reagent water.

5.2.1.1. Prepare the spike standard solution by dissolving 3.819 g of NH_4Cl in reagent water and dilute to 1 L with additional reagent water.

5.2.1.2. The standard is used to prepare quality control (QC) check samples such as laboratory control samples (LCS/LCSDs).

5.2.1.3. The standard must be replaced after six months or sooner.

6. QUALITY CONTROL

6.1. Event Based Quality Control (LCS/LCSDs)

6.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD)

6.1.2. The acceptance criteria for LCS/LCSD compounds are as follows:

6.1.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤20%.

6.1.2.2. All LCS/LCSD compounds must be within acceptance limits.

7. PROCEDURE

7.1. Aqueous LCS/LCSD Sample Preparation for SM 4500-NH_3 B/C

7.1.1. For LCS/LCSD, measure 500 mL of clean reagent water.

7.1.2. Add 2.5 mL of the spike standard to each LCS/LCSD sample.

7.1.3. Add 25 mL of borate buffer solution into the sample, and adjust the pH to 9.5 with 6-N NaOH solution.

7.1.4. Add a few boiling chips into the distillation flask.

7.1.5. Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.

7.1.6. Use a specimen container containing 50 mL of indicating boric acid solution to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the indicating boric acid solution.

7.1.7. Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.

7.1.7.1. Continue distillation during the last minute or two, but lower the specimen container such that the end of the delivery tube is free of contact with the liquid to cleanse the condenser and the delivery tube.

7.1.8. Proceed to Section 7.4.

7.2. Non-Aqueous LCS/LCSD Sample Preparation for SM 4500-NH_3 B/C

7.2.1. For solid LCS/LCSD, measure 10.0 g of washed sea sand. For marine sediment LCS/LCSD, measure 250 g of washed sea sand.

7.2.2. Add 2.5 mL of the spike standard to each LCS/LCSD sample.

7.2.3. Add 500 mL of reagent water into the sample.

7.2.4. Add 25 mL of borate buffer solution into the sample, and adjust the pH to 9.5 with 6-N NaOH solution.

7.2.5. Add a few boiling chips into the distillation flask.

7.2.6. Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.

7.2.7. Use a specimen container containing 50 mL of indicating boric acid solution to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the indicating boric acid solution.

7.2.8. Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.

7.2.8.1. Continue distillation during the last minute or two, but lower the specimen container such that the end of the delivery tube is free of contact with the liquid to cleanse the condenser and the delivery tube.

7.2.9. Proceed to Section 7.4.

7.3. Aqueous LCS/LCSD Sample Preparation for EPA Method 350.2

7.3.1. For LCS/LCSD, measure 400 mL of clean reagent water.

7.3.2. Add 2.0 mL of the spike standard to each LCS/LCSD sample.

7.3.3. Adjust the pH to 9.5 with 1-N NaOH.

7.3.4. Add 25 mL of borate buffer solution into the sample.

7.3.5. Add a few boiling chips into the distillation flask.

7.3.6. Disconnect the steaming-out flask and immediately connect the sample flask to the distillation apparatus.

7.3.7. Use a specimen container containing 50 mL of absorbent solution to collect the distillate, and adjust the condenser such that the tip of the delivery tube is below the surface of the absorbent solution.

7.3.8. Distill at a rate of 6 to 10 mL/min and collect 200 mL of distillate.

7.3.9. Proceed to Section 7.5.

7.4. LCS/LCSD Sample Analysis for SM 4500-NH_3 B/C

7.4.1. Titrate by adding 0.02-N standard H_2SO_4 titrant until a pale lavender color is displayed.

7.4.2. Record the volume of standard H_2SO_4 titrant used to the nearest 0.01 mL.

7.5. LCS/LCSD Sample Analysis for EPA Method 350.2

7.5.1. Add 3 drops of mixed indicator solution to the distillate.

7.5.2. Titrate by adding 0.02-N standard H_2SO_4 titrant until a pale lavender color is displayed.

7.5.3. Record the volume of standard H_2SO_4 titrant used to the nearest 0.01 mL.

7.6. One LCS/LCSD pair is recommended every day distillations are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

8. CALCULATIONS

8.1. The recovery of LCS ammonia as nitrogen is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of ammonia as nitrogen in LCS (or LCSD).
$C_{recovered}$ = concentration of ammonia as nitrogen recovered.
C_{added} = concentration of ammonia as nitrogen added.

Note: Concentrations must be in equivalent units.

Appendix B

GENERAL INORGANIC RAW DATA FORM – MBDUP

Calscience Environmental Laboratories, Inc.

Calscience Environmental Laboratories
General Inorganic Raw Data Form – MBDUP

Analyte: ☐ Chloride, ☐ Chlorine, Free, ☐ Chlorine, Residual, ☐ Chemical Oxygen Demand (COD), ☐ Hardness Ca, ☐ Hardness, ☐ Ammonia-N, ☐ Organic Nitrogen, ☐ Total Kjeldahl Nitrogen (TKN), ☐ Oil and Grease, Total Recoverable ☐ Sulfide, ☐ Sulfite, ☐ Other (Specify) _____

MB DUP

Instructions:
1. A copy of the supporting raw data must be attached.
2. Cel ID consists of Work Order Number and Bottle/Vial ID.

METHOD	MATRIX	DATE	ANALYST(S)	BATCH NUMBER	CONC UNIT(S)	INSTRUMENT NAME / ID
		Preparation:		MB:		
		Analysis:		Sample Duplicate:		

CEL ID #	INITIAL CONC	DILUTION FACTOR	FINAL CONC	RPD	CONTROL LIMIT	COMMENTS
Sample					0 – 25	
Duplicate						

CEL ID #		TIME START	TIME END	SAMPLE INITIAL WEIGHT / VOLUME	SAMPLE FINAL VOLUME	SAMPLE DILUTION FACTOR	SAMPLE PREP FACTOR	SAMPLE FINAL FACTOR	INITIAL CONC	FINAL CONC	RL	QUALIFIER	COMMENTS
MB	Method Blank												
Duplicate													

Title : **SM 4500-O G: DISSOLVED OXYGEN, MEMBRANE ELECTRODE METHOD.**

Document No. : SOP-M746
Revision No. : Original
Supersedes : None

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PROPRIETARY INFORMATION STATEMENT

APPROVED FOR RELEASE BY: _____ **MANAGEMENT** 10/08/02 **DATE**

_____ **QA DEPARTMENT** 10/08/02 **DATE**

1. SCOPE AND APPLICATION

1.1. Dissolved oxygen (DO) levels in natural and waste waters depend on the physical, chemical, and biochemical activities in the water body. The analysis for DO is a key test in water pollution and waste treatment process control.

2. METHOD SUMMARY

2.1. Accurate measurement of dissolved oxygen using polarographic electrodes is commonly performed in water and wastewater laboratories. This method measures partial pressure of oxygen, rather than oxygen alone.

2.2. Partial pressure is converted into concentrations (ppm) by using the solubility value of oxygen at that specific temperature. The oxygen meter calculates these values on the basis of the known relationship between oxygen solubility, temperature and total atmospheric pressure.

3. COMMENTS AND INTERFERENCES

3.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. Each analyst must demonstrate the ability to generate acceptable results and be approved by the applicable Group Leader prior to analyzing billable samples.

4. HAZARDS AND PRECAUTIONS

4.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

4.2. Exposure to chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, safety glasses and lab coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

4.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

5. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

5.1. Samples should be collected in glass containers, and if at all possible, in BOD bottles with stopper.

5.2. Collector should avoid entraining or dissolving atmospheric oxygen by preventing turbulence and formation of bubbles while collecting sample.

5.3. Samples must be analyzed as soon as possible following collection. Protect stored samples from strong sunlight.

5.4. Matrix-based quality control measures may require additional sample quantities.

5.5. Additional sample handling information can be found in the Sample Control SOPs.

6. APPARATUS AND MATERIALS

6.1. Dissolved Oxygen Meter, Orion Model 850, or equivalent

6.2. BOD bottles, 300ml, glass, with stopper.

7. REAGENTS AND STANDARDS

7.1. REAGENT WATER: Deionized, distilled, interferant-free.

8. PROCEDURE

8.1. INSTRUMENT CALIBRATION

8.1.1. Calibration must be performed each day prior to sample analysis.

8.1.2. Allow the probe to polarize 30-50 minutes BEFORE attempting calibration of the electrode.

8.1.3. Prepare a BOD bottle with 50 ml of distilled water as the standard. Be sure to use the funnel accessory. Place the electrode in the funnel so it is just above the stirring paddle.

8.1.4. Ensure that the water level in the bottle is ½" below the tip of the electrode.

8.1.5. Press the **CAL**ibrate key (while the unit is in the **MEASURE** mode) to enter the calibration mode. The Calibration annunciator will light up and stay lit throughout the calibration.

8.1.6. The display will now show "SP," for set point, as the prompt for the calibration standard. When "SP" is displayed and the electrode has been placed in the standard, the unit goes into a stability-checking mode while displaying "----" in the main readout.

8.1.7. Wait for the READY indicator to light. The main readout will display either the measured value based upon the last calibration, or 101.7. If the AUTOCAL function has been activated, the meter will set the calibration standard value to 101.7%. If the AUTOCAL function has been disabled, the SET point must be edited to 100%. Press YES to accept calibration. The meter will proceed to MEASURE mode.

8.1.7.1. All calibrations may be aborted by pressing the MODE key before the standard value has been entered. All calibration errors will be displayed until any key has been pressed. The calibration data will be in the following format:

CALIBRATION

MICRO AMPS AND TEMP

TIME AND DATE

8.2. SAMPLE ANALYSIS

8.2.1. Introduce the electrode into the sample, as done when calibrating the unit. Be sure to dislodge any air bubbles that may have adhered to the electrode.

8.2.2. Verify that constant stirring with turbulence takes place while the electrode is submerged in the sample. This stirring allows for the oxygen molecule transfer across the membrane.

8.2.3. When in the measuring mode, wait for the READY light to come on and record your results.

8.2.4. Record results in mg DO/L, or ppm.

9. CALCULATION

9.1. No calculations are required, as DO results are read directly from the meter display in units of ppm.

10. QUALITY CONTROL

10.1. The laboratory must, on a ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

10.2. All quality control data should be maintained and available for easy reference and inspection.

10.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 should be adhered, unless superseded in this document.

10.4. A duplicate sample shall be analyzed for every batch of 20 samples or fraction thereof. The value for the duplicate should not differ by more than 25 percent of the original value.

11. REPORTING

11.1. Reporting limit: 0.01 mg DO/ L

11.2. The data reported must adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

12. REFERENCE

12.1. 4500-O: Oxygen (Dissolved), Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

12.2. Dissolved Oxygen Meter, Models 810 and 850 Instruction Manual, ©Copyright 1996, Orion Research, Inc.

13. **APPENDICES**

13.1. None

Title : SM 5210 B / EPA 405.1: BIOCHEMICAL OXYGEN DEMAND (5 DAY)

Document No. : SOP-M705
Revision No. : 2.3
Supersedes : 2.2 and SOP-M771 1.1 (retired)

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PROPRIETARY INFORMATION STATEMENT

Revision 2.3 changes are noted in bold italicized typeface and preceded by a "▸" marker.

APPROVED FOR RELEASE BY: R. Lane — 12/04/13
MANAGEMENT — **DATE**

QA — 12-04-13
QA DEPARTMENT — **DATE**

1. ►METHOD IDENTIFICATION

1.1. SM 5210 B / ***EPA 405.1***: Biochemical Oxygen Demand (5 Day)

2. ►APPLICABLE MATRICES

2.1. Municipal and industrial wastewaters, effluents and polluted waters.

2.2. ***Soil, solid and non-aqueous matrices may be analyzed using the extraction procedure noted in Section 14.3. and reporting as a modified method, EPA Method 405.1(M) or SM 5210 B(M)***

3. ►DETECTION LIMITS

3.1. The lowest detection limit ***is 1.0*** mg/L ***for aqueous samples and 5.0 mg/kg for solid samples***.

4. ►SCOPE AND APPLICATION

4.1. This biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters, effluents and polluted waters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water.

4.2. Demand may be analyzed and reported as total (carbonaceous and nitrogenous) or speciated. Carbonaceous BOD (CBOD), separate from nitrogenous, may be determined by the addition of a nitrification inhibitor, i.e., 2-chloro-6-(trichloro methyl) pyridine ***(TCMP)***.

4.3. The working range of the method is maximum initial DO (between 7 and 9 mg/L) and minimum residual DO of 1 mg/L, multiplied by the dilution factor.

5. METHOD SUMMARY

5.1. The BOD test is an empirical bioassay-type procedure that measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present in a sample. The standard test conditions include dark incubation at 20°C ± 1°C for a specified period of 5 days. The reduction in the dissolved oxygen (DO) concentration during the incubation period yields a measure of the biochemical oxygen demand.

5.2. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method, and the interpretation of the outputs thereof. Each analyst who performs this test must demonstrate the ability to generate acceptable data with this method and be authorized by the applicable Group Leader prior to reporting results from analyses of client samples.

6. ▶DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.10. ***Limit of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility***.

6.11. ***Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence***.

6.12. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.13. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.14. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.15. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.16. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.17. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.18. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.19. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.20. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.21. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.22. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.23. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. ►INTERFERENCES

7.1. Significant sample degradation may occur rapidly following sampling, resulting in low BOD values. Samples should be transported cooled and analysis should begin within ***48*** hours of collection.

7.2. The ground-glass water seal between the BOD bottle and the cap must remain intact during incubation to prevent air contamination.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, protective eyewear (e.g., safety glasses or faceshield) and apparel (e.g., lab coat or apron) are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDS) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. BOD Reader: Automated, ThermoAutomation, or equivalent.

9.2. Dissolved oxygen meter with membrane electrode. Checked periodically using Modified Winkler Method for DO.

9.3. ***Instrument Software***

9.3.1. ***Not applicable.***

9.4. ***Instrument Maintenance and Troubleshooting***

9.4.1. ***Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.***

9.4.2. ***Additional information can be found in the user manual or operating guide for the specific instrument.***

9.5. Incubator Oven capable of maintaining 20 ± 1°C. Exclude all light to prevent possible photosynthetic production of DO.

9.6. Incubation bottles: 300-mL capacity. Clean bottles with detergent, rinse thoroughly, and drain before use.

9.7. Graduated cylinder: 500-mL, other volumes as necessary, glass, class A.

9.8. Volumetric pipets: 5, 10-mL, other volumes as necessary, glass, class A.

9.9. Volumetric flasks: 1-L, 500-mL, other volumes as necessary, glass, class A.

9.10. Parafilm or equivalent moisture barrier.

9.11. Aluminum foil to create a light shield and prevent photo-oxidation of the samples.

9.12. ***Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.***

9.13. ***Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.***

10. ►REAGENTS AND STANDARDS

10.1. ***Reagents***

10.1.1. Reagent water: Interferant-free water supplied from in-house 18megohm Nanopure system.

10.1.2. ***Sand, washed, sea or standard Ottawa.***

10.1.3. ***Potassium phosphate monobasic, KH_2PO_4, reagent grade or equivalent.***

10.1.4. ***Potassium phosphate dibasic, K_2HPO_4, reagent grade or equivalent.***

10.1.5. ***Sodium phosphate dibasic heptahydrate, $Na_2HPO_4 \bullet 7H_2O$, reagent grade or equivalent.***

10.1.6. ***Ammonium chloride, NH_4Cl, reagent grade or equivalent.***

10.1.7. Phosphate buffer solution:

10.1.7.1. Dissolve 8.5g of KH_2PO_4, 21.75g K_2HPO_4, 33.4g $Na_2HPO_4 \bullet 7H_2O$ and 1.7g NH_4Cl in 500 mL reagent water and dilute to 1L. The solution should be approximately 7.2 pH units. Discard reagent if there is noticeable sign of biological growth ***and/or precipitation occurs***.

10.1.8. ***Magnesium sulfate heptahydrate, $MgSO_4 \bullet 7H_2O$, reagent grade or equivalent.***

10.1.9. Magnesium sulfate ($MgSO_4$) solution:

10.1.9.1. Dissolve 22.5g of $MgSO_4 \bullet 7H_2O$ in 500 mL reagent water and dilute to 1L.

10.1.10. ***Calcium chloride, $CaCl_2$, reagent grade or equivalent.***

10.1.11. Calcium chloride ($CaCl_2$) solution:

10.1.11.1. Dissolve 27.5g of $CaCl_2$ in 500 mL reagent water and dilute to 1L.

10.1.12. ***Ferric chloride hexahydrate, $FeCl_3 \bullet 6H_2O$, reagent grade or equivalent.***

10.1.13. Ferric chloride ($FeCl_3$) solution:

10.1.13.1. Dissolve 0.25g of $FeCl_3 \bullet 6H_2O$ in 500 mL reagent water and dilute to 1L.

10.1.14. ***Sulfuric acid, concentrated, H_2SO_4, reagent grade or equivalent.***

10.1.15. Neutralization acid solution:

10.1.15.1. Slowly and while stirring, add 28mL of sulfuric acid to reagent water and dilute to 1 L.

10.1.16. ***Sodium hydroxide, NaOH, reagent grade or equivalent.***

10.1.17. Neutralization alkali solution:

10.1.17.1. Dissolve 40g of sodium hydroxide in 500 mL reagent water and dilute to 1 L.

10.1.18. ***Sodium sulfite, Na_2SO_3, reagent grade or equivalent.***

10.1.19. Sodium sulfite (Na_2SO_3) solution:

10.1.19.1. Dissolve 1.575g of Na_2SO_3 in 500 mL reagent water and dilute to 1 L.

10.1.19.2. This solution is not stable and must be prepared daily.

10.1.20. Potassium Iodide (KI)-Starch test strips: Fisher 14-860, or equivalent.

10.1.21. Nitrification inhibitor: 2-chloro-6-(trichloromethyl) pyridine, 2.2% TCMP, Hach 2579-24, or equivalent.

10.1.22. Seed Source: InterLab Polyseed BOD_5 Seed Inoculum, or equivalent.

10.1.23. ***Glucose, $C_6H_{12}O_6$, reagent grade or equivalent.***

10.1.24. ***Glutamic acid, $C_5H_9NO_4$, reagent grade or equivalent.***

10.1.25. Glucose-glutamic acid solution:

10.1.25.1. Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 hr.

10.1.25.2. Add 150 mg glucose and 150 mg glutamic acid to reagent water and dilute to 1 L.

10.1.25.3. Prepare fresh immediately before use.

10.1.26. Dilution water:

10.1.26.1. Place desired volume of water in a suitable bottle and add phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions at a rate of 1 mL each/liter of water prepared.

10.1.26.2. The DO uptake should not be more than 0.2 mg/L, and preferably, below 0.1 mg/L.

10.1.27. ***All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. ***Standards***

10.2.1. ***None.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Samples should be collected in 1-L glass or polyethylene containers. For visually clear waters, a 500-mL sample should be sufficient for testing.

11.2. ***Samples should be maintained in a chilled state, 0-6°C, not frozen, post sample collection until received at the laboratory, where they are stored under refrigerated conditions.***

11.3. If analysis commences within 2 hours of collection, cold storage is unnecessary.

11.4. Analysis must begin within ***48*** hours of collection.

11.5. Additional sample handling information can be found in ***the Sample Control SOPs.***

12. QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. All quality control data should be maintained and available for easy reference and inspection.

12.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 should be adhered, unless superseded in this document.

12.4. There is no measurement for establishing bias of the BOD procedure. The following checks are intended to provide a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique.

12.5. Summary of QC Checks

12.5.1. Seed Control

12.5.1.1. Three Seed Controls are analyzed for each batch, not to exceed 20 samples.

12.5.1.2. The DO uptake of the seeded dilution water should be between 0.6 and 1.0mg/L.

12.5.2. Sample Duplicate

12.5.2.1. One Sample Duplicate, at a minimum, is analyzed for each batch, not to exceed 20 samples.

12.5.3. Dilution Water Blank

12.5.3.1. A blank prepared from dilution water is used as a preliminary check of the quality of the unseeded dilution water and cleanliness of the incubation bottles. One Dilution Water Blank is analyzed for each batch, not to exceed 20 samples.

12.5.3.2. The DO uptake should not be more than 0.2mg/L and preferably below 0.1mg/L. If DO uptake is above 0.2mg/L, the source water must be replaced with water of sufficient purification to pass this water check.

12.5.4. Glucose-Glutamic Acid Control

12.5.4.1. Because the BOD test is a bioassay its results can be influenced greatly by the presence of toxicants or by use of poor seeding material. A check of the seed effectiveness and analytical technique is made by BOD measurement of the glucose-glutamic acid solution. One Glucose-Glutamic Acid Control is analyzed for each preparation batch.

12.5.4.2. The following statistical information is based upon an interlaboratory study sourced from SM 5210 B. For the 300mg/L mixed primary standard, the average 5-day BOD is 198mg/L with a standard deviation of 30.5mg/L.

12.5.5. Additional information regarding internal quality control checks is provided in SOP-T020.

12.6. Corrective Action

12.6.1. The analyst must immediately inform the Group Leader of all out of control situations for specific handling instructions.

12.6.2. Event must be documented in detail on an "Out of Control Corrective Action" form and reviewed by the Group Leader. The Group Leader shall implement corrective action, list the specific procedures employed and their outcome on the corrective action form.

12.6.3. A copy of the completed Out of Control Corrective Action form must be included with all affected data packages.

12.6.4. The Group Leader should consult with the Technical Manager and/or Quality Control Manager regarding procedural inquiries and recommendations for method modification.

12.6.5. Management and the QA department as documented in a revised SOP approve modifications to the analytical process.

12.6.6. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. ***Analytical Balance***

13.1.1. ***Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.1.2. ***If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.2. ***Top Loading Balance***

13.2.1. ***Calibrate the top loading balance at 1 g and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.***

13.2.2. ***If control limits are not specified, calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.***

13.3. ***BOD Reader***

13.3.1. Turn on the BOD reader, and allow it to warm up for a minimum of 15 minutes prior to use.

13.3.2. Open the Manual Controller window and click SET GAIN.

13.3.3. Enter the calibration value and click OK.

13.3.4. The BOD reader will display the calibration results in millivolts (mV).

NOTE: The BOD probe should have a mV reading of ≥1000 to obtain an acceptable calibration.

13.3.5. Click READ DO to ensure a stable DO reading. This should last for 5 minutes.

NOTE: Continue to click READ DO until the DO reading is stable.

13.3.6. After 5 minutes, click SET GAIN again and enter the calibration value. Click OK. The BOD reader will display calibration results (in mV).

13.3.7. If the calibration is acceptable, click EXIT and save the calibration.

NOTE: The BOD reader will require recalibration each time the instrument is turned off, or each time the program is exited

14. ▶PROCEDURE

14.1. Seed Source Preparation

14.1.1. Prepare Polyseed by emptying the contents of 1 capsule into 500 mL of dilution water. Discard the gelatin capsule. Rehydrate cultures by stirring and aerating the Polyseed solution for 1 hr. Continue to stir until ready to use the Polyseed solution. Allow the solution to settle and use the supernatant as the seed. Add 2 mL of seed to all blank, environmental and QC samples.

14.1.2. To the first of three seed control bottles, add 6 mL of the Polyseed solution. Mark this bottle "Seed Control 6."

14.1.3. To the second of the three seed control bottles, add 9 mL of the Polyseed solution. Mark this bottle "Seed Control 9."

14.1.4. To the third of the three seed control bottles, add 12 mL of the Polyseed solution. Mark this bottle "Seed Control 12."

14.1.5. The DO uptake of the seeded dilution water should be between 0.6 mg/L and 1.0 mg/L. DO uptake above and below this range may result in low-biased and high-biased data, respectively.

14.2. Sample Pretreatment

14.2.1. Neutralize samples to pH 6.5 to 7.5 with the acid or alkali neutralization solutions, as necessary. Do not dilute samples ***by*** more than 0.5%.

14.2.2. Check samples for residual chlorine using a KI-Starch test strip. In some samples chlorine will dissipate within 1-2hr of standing in light. This often occurs during sample transport and handling.

14.2.2.1. If no detectable residual chlorine is present, seed the dilution water.

14.2.2.2. If residual chlorine is present, dechlorinate sample by adding a small aliquot of the Na_2SO_3 solution (see ***10.1.19***). Mix, and after 10-20min recheck for residual chlorine. Repeat until no residual chlorine is detected. Seed the dilution water.

14.2.3. Industrial materials containing plating wastes, toxic metals, and other toxic substances often require special study and treatment.

14.2.4. Samples supersaturated with DO (containing more than 9mg/L DO at 20°C) may be encountered in cold waters or in waters where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing samples to about 20°C in a partially filled bottle while agitating by vigorous shaking, or by aerating with clean filtered compressed air.

14.2.5. Bring samples to 20 ± 1°C before making dilutions.

14.2.6. If carbonaceous demand (CBOD) is desired, nitrification must be inhibited by the addition of 3 mg nitrification inhibitor to each 300mL bottle before capping. Final concentration is 10mg/L.

14.3. ***Solid Sample Preparation***

14.3.1. ***The amount to be used depends upon the type of solid matrix. Weigh out the appropriate amount, based on the table below:***

Matrix	Mass to be Used
"Clean" (sand, etc.)	2 - 5 g
"Normal" (soil, etc.)	2 - 5 g
"Dirty" (mud, silt, etc.)	0.5 g

14.3.2. ***Place weighed sample in a clean incubation bottle.***

14.3.3. ***Add 50 mL reagent water.***

14.3.4. ***Add 2 mL of the Polyseed solution.***

14.3.5. ***Follow procedure for aqueous samples beginning with step 14.4.5.***

14.4. Dilution Technique

14.4.1. Make several dilutions of prepared samples. Dilutions that result in a residual DO of at least 1mg/L and a DO uptake of at least 2mg/L after 5 day incubation produce the most reliable results. Experience with a particular sample will permit use of a smaller number of dilutions. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions.

14.4.2. In the absence of prior knowledge, the following dilutions may be used as a guide:

Type Matrix	Sample
Strong industrial wastes	0.0 to 1.0%
Raw and settled wastewater	***1 to 5%***
Biologically treated effluent	5 to 25%
Polluted river water	25 to 100%

14.4.3. Add 2 mL of the Polyseed solution to BOD bottles containing 50 mL dilution water.

14.4.4. To each of the seeded BOD bottles add the appropriate volumes of sample.

14.4.5. Using dilution water, bring the seeded sample solution to a 300 mL final volume.

14.5. Determination Of Initial Do

14.5.1. Create a worksheet by clicking FILE and then select NEW.

14.5.2. Click WORKSHEET and enter the seed name on the header.

14.5.3. Click SINGLE SAMPLE ENTRY FORM. Enter blanks, seed controls, standards and samples.

14.5.4. Save the worksheet, then load into the sample trays, the bottles for blanks, seed controls, standards, and samples.

14.5.5. Click READER, then select READ DO.

14.5.6. Click INITIAL DO, then select the sample set to be processed, and enter the number of rows to be processed.

14.5.7. Click CONTINUE. The BOD reader will begin to measure the initial DOs in the bottles designated for blanks, seed controls, standards and samples.

14.5.8. After the reader has completed the specified number of DO measurements, either select UPDATE WORKSHEET if DO readings are acceptable, or DISCARD RESULTS if the DO readings are not acceptable.

NOTE: If UPDATE WORKSHEET is selected the worksheet is updated. However, if DISCARD RESULTS is selected, all of the results currently displayed on the screen will be removed. In the latter case, the analyst must then reanalyze the samples.

14.5.9. Save the worksheet before exiting the program.

14.6. Incubation

14.6.1. Stopper bottles tightly and water-seal. It is very important that the water seal stay intact throughout the entire incubation period to prevent contamination by air. Evaporation of water seal is minimized by placing a piece of Parafilm, or equivalent barrier, over the water seal during the incubation period.

14.6.2. Incubate bottle in a temperature-***controlled*** oven for 5 days ± ***6 hours*** at 20 ± 1°C.

14.6.3. Following the 5-day incubation period, remove bottle and verify that no air bubbles exist in the bottle. If an air bubble(s) is found, the bottle is deemed contaminated and any subsequent BOD measurement unreliable. The bottle must be re-prepared and incubation repeated.

14.7. Determination Of Final Do

14.7.1. Following completion of incubation and water seal inspection, determine the final DO.

14.7.2. Calibrate the BOD reader by following the procedure under CALIBRATION (Section 13).

14.7.3. Recall the pertinent worksheet by selecting FILE, and open the worksheet.

14.7.4. Load blanks, seed controls, standards and samples into the sample trays.

14.7.5. Click READER, then select READ DO.

14.7.6. Click FINAL DO, then select the sample set to be processed, and enter the number of rows to be processed.

14.7.7. Click CONTINUE. The BOD reader will begin to measure the final Dos in the bottles designated as blanks, seed controls, standards and samples.

14.7.8. After the reader has completed the specified number of DO measurements, either select UPDATE WORKSHEET if DO readings are acceptable, or DISCARD RESULTS if the DO readings are not acceptable.

NOTE: If UPDATE WORKSHEET is selected the worksheet is updated. However, if DISCARD RESULTS is selected, all of the results currently displayed on the screen will be removed. In the latter case, the analyst must then reanalyze the samples.

14.7.9. Save worksheet before exiting the program.

NOTE: The worksheet contains BOD results of blanks, seed controls, standards and samples.

15. ▸CALCULATIONS

15.1. The BOD is calculated as follows:

$$BOD_5 = \frac{\left[(D_1 - D_2) - (B_1 - B_2)f\right] \times V_T}{V_S}$$

where:
BOD_5 = 5 day biochemical oxygen demand
D_1 = Initial DO of sample (mg/L)
D_2 = Final DO of sample (mg/L)
B_1 = Initial DO of seed control (mg/L)
B_2 = Final DO of seed control (mg/L)
f = Volume of seed in diluted sample/Volume of seed in seed control
V_S = Volume of sample used
V_T = Total volume of BOD dilution bottle

15.2. If more than one sample dilution meets the criteria of a residual DO of at least 1mg/L and a DO depletion of at least 2mg/L and;

- There is no evidence of toxicity at higher sample concentrations
- The existence of an obvious anomaly
- The sample dilutions are within 30% of the largest sample volume aliquot with acceptable depletion.

Then average the results of all acceptable data.

15.3. If no data ***meet*** the criteria, report result from the largest sample aliquot, provided it is above a residual D.O. of 1.0 mg/L.

15.4. If all sample dilutions are below residual D.O. of 1.0 mg/L, then using the highest sample dilution, calculate a greater than value as an estimation of the BOD result. Alternately, with prior client approval, the BOD analysis may be reprocessed after recommended holding time.

15.5. Report analytical results as BOD in mg/L. If nitrification inhibitor is used, report results as CBOD in mg/L.

15.6. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air-purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ***The*** concentration of target analytes in a MB should be ≤ ½ the respective reporting limits (RLs). If the concentration of any target analyte exceeds ½ its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination.

Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. Additional information regarding internal quality control checks is provided in SOP-T020.

18.4. All concentrations shall be reported in mg/L (ppm) for water samples and mg/kg (ppm) for oil, soil and solid waste samples.

18.5. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a closed-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. ►REFERENCES

22.1. *5210 B: 5-Day Biochemical Oxygen Demand,* Standard Methods for the Examination of Water and Wastewater, 21st edition, 2005 ***(Committee approval 2001)***.

22.2. ***5210 B: 5-Day Biochemical Oxygen Demand, Standard Methods for the Examination of Water and Wastewater, 22nd edition, 2012 (Committee approval 2001 / Edited 2011)***.

22.3. ***"Biochemical Oxygen Demand,"* Method 405.1 (5 Days, 20°C); SW-846, Methods for Chemical Analysis of Water and Wastes, SW-846, Revised March, 1983**.

22.4. *"Polyseed BOD_5 Seed Inoculum Application Procedure,"* InterLab, Inc.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ***Appendix A: Additional Quality Control Criteria for Department of Defense Projects***.

24. ►*MODIFICATIONS*

24.1. The following modifications to SM 5210 B are noted.

24.1.1. None.

24.2. The following modifications to EPA Method 405.1 are noted

24.2.1. *None.*

25. ►*REVISION HISTORY*

Revision	Description	Author	Effective Date
2.3	Section 1: Update method identification. Section 2: Update matrices. Section 3: Update detection limits. Section 4: Update scope and application. Section 6: Update definitions. Section 7: Update interferences. Section 9: Update equipment. Section 10: Update reagents and standards. Section 11: Update sample storage. Section 13: Update calibration. Section 14: Update procedure. Section 15: Update calculations. Section 18: Update data assessment. Section 22: Update references. Section 23: Add appendix. Section 24: Add Modifications. Section 25: Add Revision History.	K. Burney	12/16/2013

►*Appendix A*

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. ***SM 5210 B / EPA 405.1: Biochemical Oxygen Demand (5 Day) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.***

2. SCOPE AND APPLICATION

2.1. ***The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.***

3. STANDARDS

3.1. ***The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.***

4. QUALITY CONTROL

4.1. ***Limit of Detection (LOD)***

4.1.1. ***LOD determination shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.***

4.1.2. ***LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.***

4.1.2.1. ***LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit.***

4.1.2.2. ***LOD verification is deemed valid if the apparent signal-to-noise ratio of the analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., second column confirmation, pattern recognition, etc.).***

4.1.2.2.1. ***For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.***

4.1.2.3. ***If these criteria are not met, perform either one of the following tasks.***

4.1.2.3.1. ***Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.***

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. ***No samples shall be analyzed without a valid LOD.***

4.2. ***Limit of Quantitation (LOQ)***

4.2.1. ***LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.***

4.2.1.1. ***The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.***

4.2.1.2. ***The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.***

4.2.2. ***LOQ verification must be performed quarterly to verify precision and bias at the LOQ.***

4.2.2.1. ***LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.***

4.2.2.2. ***LOQ verification is deemed valid if the recovery of the analyte is within the established test method acceptance criteria or client data objectives for accuracy.***

4.3. ***Event Based Quality Control (LCS and MBs)***

4.3.1. ***Laboratory Control Sample (LCS)***

4.3.1.1. ***The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control."***

4.3.1.1.1. Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

4.3.1.2. ***The LCS shall be analyzed at a minimum frequency of one per preparation batch.***

4.3.1.2.1. In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

4.3.1.3. ***The concentration of the spiked compounds shall be at the project-specific concentration of concern. If this is not specified, it shall be at or below the midpoint of the calibration curve.***

4.3.2. ***Method Blanks (MBs)***

4.3.2.1. ***The method blank is used to assess the preparation batch for possible contamination during the preparation and processing steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated.***

4.3.2.1.1. ***Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.***

4.3.2.2. ***The method blank shall be analyzed at a minimum of 1 per preparation batch.***

4.3.2.2.1. ***In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.***

4.3.2.3. ***The MB is considered to be contaminated if one of the following conditions is met.***

4.3.2.3.1. ***The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).***

4.3.2.3.2. ***The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).***

4.3.2.3.3. ***The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).***

4.3.2.4. ***If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.***

4.3.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.4. ***Matrix Based Quality Control (Sample Duplicates)***

4.4.1. ***Sample duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method.***

4.4.1.1. ***The sample duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.***

4.4.2. ***The frequency of the analysis of sample duplicates may be determined as part of a systematic planning process (e.g., Data Quality Objectives) or as specified by the mandated test method.***

4.4.3. ***Each preparation batch of samples must contain an associated sample duplicate using the same matrix collected for the specific DoD project.***

4.4.3.1. ***In those instances for which no separate preparation method is used, the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.***

4.4.4. ***The results from sample duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments..***

4.4.5. ***Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits.***

4.4.5.1. ***For sample duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.***

5. REFERENCES

5.1. ***Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.***

Title : **SM 5310 B/D / EPA METHOD 415.1, TOTAL ORGANIC CARBON (TOC)**

Document No. : SOP-M726
Revision No. : 1.3
Supersedes : 1.2

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PROPRIETARY INFORMATION STATEMENT

Revision 1.3 changes are noted in bold italicized typeface and preceded by a "▸" marker.

APPROVED FOR RELEASE BY: _____ 02/24/15
MANAGEMENT **DATE**

_____ 02-24-15
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. SM 5310 B/D / EPA Method 415.1, Total Organic Carbon (TOC).

2. APPLICABLE MATRICES

2.1. This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes.

3. DETECTION LIMITS

3.1. The estimated quantitation limits EQLs for this method are approximately 0.5mg/L for aqueous samples. The EQLs will be proportionally higher for samples which require dilution.

4. SCOPE AND APPLICATION

4.1. This method is applicable only to samples which can be prepared homogeneously and loaded onto the TOC analyzer reproducibly.

5. METHOD SUMMARY

5.1. Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

5.2. Catalytic Combustion:

5.2.1. The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst (i.e. platinum group metals). The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is transferred in the carrier-gas streams and is measured separately by means of a non-dispersive infrared (NDIR) detector. The NDIR detector is calibrated to display the mass of CO_2 detected.

5.2.2. Because total carbon is measured, inorganic carbon must be removed by acidification and sparging and the TOC obtained by difference. This is typically done automatically by the instrument based upon whether the TIC or TOC option is selected.

5.3. Wet Chemical Oxidation:

5.3.1. The sample is acidified with phosphoric acid to convert carbonate and bicarbonate ions into dissolved CO_2. This CO_2 is purged from solution, concentrated by trapping, then desorbed and carried into a non-dispersive infrared (NDIR) analyzer which has been calibrated to directly display the

mass of CO_2 detected. This mass is equivalent to the mass of total inorganic carbon (TIC) in the sample.

5.3.2. After the sample has been acidified and purged of TIC, sodium persulfate ($Na_2S_2O_8$), a strong oxidizer, is added. $Na_2S_2O_8$ quickly reacts with organic carbon in the sample at 100°C to form CO_2. When the oxidation reaction is complete, the CO_2 is purged from the solution, concentrated by trapping, and detected similarly as in the determination for TIC. The resulting carbon mass in the form of CO_2 is equivalent to the mass of total organic carbon (TOC) originally present in the sample.

6. DEFINITIONS

6.1. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.2. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.3. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.4. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.5. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.6. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.7. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.8. Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or

analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.9. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.10. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.11. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.12. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.13. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.14. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.15. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets user needs.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes

which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. TERMS SPECIFIC TO TOC ANALYSIS

6.21.1. Total Carbon (TC): All of the carbon in a sample, including inorganic, organic, and volatile carbon.

6.21.2. Total Inorganic Carbon (TIC): All of the carbon in a sample that is converted to carbon dioxide after sample acidification. TIC includes all dissolved carbon dioxide, bicarbonate, and carbonate species.

6.21.3. Total Organic Carbon (TOC): All of the carbon in a sample including purgeable compounds that is converted to carbon dioxide by oxidation. TOC is determined by acidifying the sample to remove the TIC and oxidizing the remaining carbon.

7. INTERFERENCES

7.1. Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

7.2. Method interferences, which are positive biases, may be caused by contaminants in the gas, dilution water, reagents, glassware, or other sample processing equipment. All of these materials must be routinely demonstrated to be free from interference under the conditions of analysis by running reagent blanks.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals and samples.

8.2. Dilute acids are prepared in this procedure. Wear appropriate glasses, coats, and gloves when handling acids and always add acid to water to limit the exothermic reaction. Heat will be generated.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Total Organic Carbon Analyzer: OI Analytical Model 1010 TOC Analyzer configured with Model 1051 Autosampler and PC based data system or equivalent.

9.1.1. Sample loop, 5-mL.

9.1.2. Autosampler vial, clear glass, 40mL (95.25mm × 27mm), disposable. Vial is equipped with open-hole screw cap and Teflon-faced septum.

9.2. Total Organic Carbon Analyzer: OI Analytical Model 1020A TOC Analyzer configured with Model 1051 Autosampler and PC based data system or equivalent.

9.2.1. Sample loop, 200-µL (nominal).

9.2.2. Autosampler vial, clear glass, 40mL (95.25mm × 27mm), disposable. Vial is equipped with open-hole screw cap and Teflon-faced septum.

9.3. Calibrated analytical balance, capable of weighing to 0.1 mg.

9.4. Drying oven capable of maintaining a temperature of 110°C (for drying the KHP).

9.5. Volumetric flask, Class "A", 10-mL, 50-mL, 100-mL, 250-mL, and 1-L, or other volumes as needed.

9.6. Pipetter.

9.7. Weighing paper.

9.8. Calibrated dispenser, set volume to 1 mL or 2 mL.

9.9. Magnetic stirrer.

9.10. Wash bottle, 250-mL.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, distilled or deionized.

10.1.2. Sodium persulfate ($Na_2S_2O_8$), 100-g/L, reagent grade.

10.1.2.1. Prepare the solution by adding 100 g of $Na_2S_2O_8$ into a 1-L volumetric flask and diluting to volume with reagent water.

10.1.3. Phosphoric acid (H_3PO_4), 5% (v/v), reagent grade.

10.1.3.1. Prepare the solution by volume by adding 59 mL of 85% H_3PO_4 into a 1-L volumetric flask and diluting to volume with reagent water.

10.1.4. Sulfuric acid (H_2SO_4), 1:1, reagent grade.

10.1.4.1. Dilute equal volumes of concentrated sulfuric Acid with reagent water to reach a 1:1 solution. Add the acid to the water and use caution as heat will be generated.

10.2. Standards

10.2.1. Potassium biphthalate (KHP) stock standard, 1000 mg/L of carbon.

10.2.1.1. Add 2.128 g of KHP (previously dried to constant mass at 110°C) to a 1-L volumetric flask and dilute to volume with reagent water.

10.2.1.2. Prepare the calibration standards by diluting the 1000-ppm stock standard with reagent water to achieve the necessary concentrations of 0.5, 2.5, 5.0, 10, or 20ppm for the low level curve, or 0.5, 1.0, 10.0, 100, and 1000ppm for the high level curve. Use volumetric glassware to make the dilutions.

10.2.1.3. For the CCV, partially fill a 1000-mL volumetric flask with reagent water, spike 10.0 mL of the 1000-ppm stock standard the flask (or add 5.0 mL for the low level analysis) and dilute to volume with reagent water to make a 5-ppm or 10-pmm CCV standard.

10.2.2. Second source standards, 1000 mg/L of carbon. The salts used to make these standards are from a different vendor, or are different lot #s from the same vendor. The second source standard is used to prepare ICV, LCS/LCSD, and MS/MSD by diluting the second source stock standard with reagent water. Use volumetric glassware to make the dilutions.

10.2.2.1. For ICV and the LCS/LCSD, partially fill a 1000-mL volumetric flask with reagent water, spike 10.0 mL (or add 5.0 mL for the low level analysis) of the 1000-ppm second source stock standard into the flask and bring to volume with reagent water.

10.2.2.2. For MS/MSD, partially fill a 100-mL volumetric flask with the client sample, spike 1.0 mL (or add 0.5 mL for the low level analysis) of the 1000-ppm second source stock standard into the flask and bring to volume with additional sample.

10.2.2.3. ICV/LCS/LCSD, MS/MSD – Low Level TOC = 5-ppm standard.

10.2.2.4. ICV/LCS/LCSD, MS/MSD – High Level TOC = 10-ppm standard.

10.2.3. Sodium carbonate (Na_2CO_3), 1000 mg/L of carbon. This standard is applicable to Total Inorganic Carbon (TIC) analysis only.

10.2.3.1. Prepare a stock solution by adding 8.826 g of Na_2CO_3 (previously dried to constant mass at 110°C) into a 1-L volumetric flask and diluting to volume with reagent water.

10.2.3.2. Calibration standards and spikes would be prepared as for the TOC standards. Refer to Sections 10.2.1 and 10.2.2 for further information on standard preparation schemes.

10.3. Gases

10.3.1. Nitrogen gas, 4.5 grade or better.

10.3.2. Oxygen gas, Ultra high purity.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. A 250-mL amber bottle preserved with H_2SO_4 and no headspace is preferred.

11.1.1. For most accurate analyses, sampling containers should be free of organic contaminants. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. Sampling and storage of samples in amber glass bottles is preferable over plastic.

11.2. To limit oxidation and/or bacterial decomposition, samples should be maintained in a chilled state at 0–6°C and protected from sunlight and atmospheric oxygen prior to analysis.

11.3. In instances where analysis cannot be performed within 2 hours from time of sampling, the sample must be acidified to pH ≤ 2 with H_2SO_4.

11.3.1. SM 5310 D (Section 1.d): Acid preservation invalidates any inorganic carbon determination on the samples. If Total Inorganic Carbon (TIC) is required, collect a separate unpreserved aliquot.

11.4. Samples should be analyzed within 28 days from collection.

12. QUALITY CONTROL

12.1. Replicate Injections

12.1.1. Each standard or sample is introduced a minimum of two times and the percent relative standard deviation (%RSD) must be calculated.

12.1.1.1. In order for the injections to be acceptable and analysis to continue, the calculated %RSD between replicate injections must be ≤ 10%. If the %RSD criteria are met, report the average of the replicates.

12.1.2. In the event that the first two replicates do not result in a %RSD ≤ 10%, the sample must be reanalyzed in duplicate. Again, calculate the %RSD between these duplicate injections. If the %RSD criteria are met, report the average of the replicates.

12.1.3. If the second set of replicates does not meet criteria, analyze a third set of duplicate samples. Again, calculate the %RSD between these duplicate injections. If the %RSD criteria are met, report the average of the replicates. If the criteria are not met, proceed as follows:

12.1.3.1. Review all three sets of data for the lowest %RSD, be sure all associated quality control is within criteria for that data set and report the average of the replicates. Note on the Chemist's bench sheet that the %RSD was outside criteria. The data will need to be flagged and the PM will need to address the issue in the narrative.

12.1.4. If it is taking several replicate injections to meet the %RSD criteria for calibration standards and/or the LCS, stop the analysis, perform maintenance and recalibrate the instrument.

12.2. Initial Calibration (ICAL)

12.2.1. An acceptable initial calibration must be established prior to the processing of samples.

12.2.2. The calibration curve consists of a calibration blank and five calibration standards which define the calibration range.

12.2.3. The ICAL is deemed valid if the correlation coefficient of the calibration curve is ≥ 0.995.

12.2.4. If this criterion is not met, then the ICAL is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.5. At a minimum, an initial calibration must be performed annually.

12.3. Initial Calibration Verification (ICV)

12.3.1. An ICV is analyzed immediately following the initial calibration standards and is used to validate the acceptance of the ICAL. The ICAL is deemed valid if the %D of TOC in the ICV is ≤ 15%.

12.3.2. If this criterion is not met, the ICAL is deemed unacceptable for sample analysis. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibrate, if necessary.

12.3.2.1. Recalibration will be necessary if repreparation and reanalysis of a new ICV solution does not meet acceptance criteria.

12.4. Initial Calibration Blank (ICB)

12.4.1. The ICB is used to monitor the instrument baseline for carryover and/or contamination and is analyzed immediately following the ICV. The ICB is deemed satisfactory if no contaminants are detected.

12.4.2. If this criterion is not met, the analytical system is deemed unacceptable for sample analysis to begin. Determine and eliminate the source of contamination. Reanalyze the ICB. If the ICB criterion remains unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Verification (CCV)

12.5.1. Following the establishment of a valid ICAL, a CCV standard must be analyzed daily prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

12.5.2. The ICAL is deemed valid if the %D of TOC in the CCV is ≤15%.

12.5.3. If this criterion is not met, the ICAL is deemed unacceptable for sample analysis to resume. Reanalyze the CCV. If the CCV criterion remains unacceptable, effect corrective action and recalibrate.

12.5.3.1. Following recalibration and the analysis of the ICV/ICB, reanalyze all samples analyzed since the last acceptable CCV.

12.5.3.2. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

12.6. Continuing Calibration Blank (CCB)

12.6.1. CCBs are used to monitor the instrument baseline for carryover and/or contamination and are analyzed immediately following the CCVs. The CCBs are analyzed daily prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

12.6.2. The instrument baseline is deemed satisfactory if no TOC is detected in the blank above the RL or other project defined criteria.

12.6.3. If this criterion is not met, the analytical system is deemed unacceptable for sample analysis to resume. Determine and eliminate the source of contamination. Reanalyze the CCB. If the CCB criterion remains unacceptable, effect corrective action and recalibrate.

12.7. Event Based Quality Control (LCS/LCSDs and MBs)

12.7.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample, laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.7.2. The acceptance criteria for LCS/LCSD compound(s) are as follows:

12.7.2.1. The lower and upper acceptance limits for %REC of TOC in the LCS/LCSD are 80% and 120% respectively. The RPD is ≤ 20%.

12.7.3. Ideally, the concentration of the target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of the target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.7.3.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB without qualification.

12.7.3.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment must be exercised to determine if the data should be qualified, or rejected and the samples re-analyzed.

12.8. Matrix Based Quality Control (MS/MSDs)

12.8.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD).

12.8.2. The acceptance criteria for MS/MSD compound(s) are as follows:

12.8.2.1. The lower and upper limits for %REC of TOC in the MS/MSD are 75% and 125% respectively. The RPD is ≤ 25%.

12.8.2.2. When the %REC and RPD of the MS/MSD compound are at or within acceptance limits, the analytical system is deemed to be in control for the particular sample and/or matrix.

12.8.2.3. If the %REC and/or RPD of the MS/MSD compound are not within the established acceptance limits, the analytical system performance shall be suspect.

12.8.2.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance. Unacceptable RPD values are typically caused by sample in-homogeneity or poor instrument performance. To evaluate the performance of the analytical system, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference in the associated MS/MSD.

12.9. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data is invalidated and all associated samples re-analyzed.

12.10. Additional information regarding internal QC checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Calibrate the instrument according to the instrument manufacturer's recommended procedures, using the calibration standard solutions. To minimize erratic readings, the system is programmed to average duplicate readings.

13.1.1. Replicate injections must have an RSD of ≤ 10%.

13.1.2. Prior to the analysis of samples, a valid initial five-point calibration curve must be established. There are two curves, one for high-level samples and one for low-level samples. In both cases a calibration blank must also be analyzed and included in the curve.

13.1.2.1. The calibration blank standard of 0.0ppm carbon is obtained by analyzing a calibration blank. The calibration blank consists of reagent water.

13.1.2.2. The concentrations of the calibration standards are 0.5, 2.5, 5.0, 10.0, and 20.0ppm of carbon for low-concentration analysis.

13.1.2.3. The concentrations of the calibration standards are 0.5, 1.0, 10.0, 100, and 1000ppm of carbon for high-concentration analysis.

13.1.3. Using linear regression curve fitting, calculate the correlation coefficient (r). The calibration curve is deemed acceptable if $r \geq 0.995$.

13.2. A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

13.2.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

13.3. Analytical Balance

13.3.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.3.2. Calibration shall be within ± 10% at 2 mg (± 0.2 mg), or within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.4. Pipetter

13.4.1. Calibrate the pipetter according to the procedure outlined in the Pipetter Calibration Check Logbook.

13.5. Dispenser

13.5.1. Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.

14. PROCEDURE

14.1. Clean Water Recycling

14.1.1. Clean water recycling must be performed daily prior to sample analysis to eliminate carbon contamination. To do this, load ten (10) autosampler vials containing reagent water onto the sample tray and commence the clean water recycling sequence.

14.2. Fill each autosampler vial with the appropriate instrument or sample QC.

14.2.1. For ICV (when calibrating), fill the vial with the appropriate spiked sample.

14.2.2. For CCV, fill the vial with the appropriate spiked sample.

14.2.3. For IB / CCB / MB, fill the vial with reagent water.

14.2.4. For LCS / LCSD, fill the vial with the appropriate spiked sample.

14.2.5. For MS / MSD, fill the vial with the appropriate spiked sample.

14.3. The autosampler vials are loaded onto the sample tray and analyzed in the following or other logical order:

Instrument Blank

*Calibration standard 1

*Calibration standard 2

*Calibration standard 3

*Calibration standard 4

*Calibration standard 5

*Initial Calibration Verification (ICV)

*Initial Calibration Blank (ICB)

Continuing Calibration Verification (CCV)

Continuing Calibration Blank (CCB)

Method Blank (MB)

Laboratory Control Sample (LCS)

Laboratory Control Sample Duplicate (LCSD)

Samples (up to 20 per batch)

Matrix Spike (MS)

Matrix Spike Duplicate (MSD)

Ending (or bracketing) CCV

Ending (or bracketing) CCB

14.3.1. An instrument blank is analyzed prior to the analysis of any samples or standards to show that the instrument baseline is clean and stable.

14.3.2. *ICAL standards 1-5, ICV and ICB are analyzed whenever the instrument needs calibration due to failing CCVs and/or major instrument maintenance that results in recalibration being necessary.

14.3.3. A CCV is used to verify the acceptance of the initial four-point calibration on a continuing basis. An acceptable CCV is required prior to sample analysis, every 20 samples thereafter, and at the end of every sequence.

14.3.3.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

14.3.4. A CCB is used to verify the acceptability of instrument baseline and to isolate sources of contamination in the MB that may occur. An acceptable CCB is required prior to sample analysis, every 20 samples thereafter, and at the end of every sequence.

14.3.5. The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used. The MB consists of reagent water.

14.3.5.1. One MB is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.3.6. An LCS is a known matrix which has been spiked with a known concentration of the target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used. The LCS consists of the target analyte spiked into reagent water.

14.3.7. An LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.4.

14.3.7.1. One LCS/LCSD pair is required for every batch of 20 samples per matrix or portion thereof.

14.3.8. Up to 20 samples per batch. If the instrument response is or suspected to be above its calibration range, samples should be sufficiently diluted to ensure that the TOC analyzer is not contaminated. In diluting, increased reporting limits may result.

14.3.9. An MS is the actual matrix spiked with a known concentration of the target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.3.9.1. The purpose of an MS is to assess the effect of a sample matrix on the recovery of the target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.3.

14.3.9.2. One MS is required for every batch of 20 samples per matrix or portion thereof analyzed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.3.10. An MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.3.11. An acceptable CCV and CCB are required at the completion of every analytical sequence.

14.4. Set up the TOC analyzer in preparation for the analytical sequence.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record the pertinent information in the run logbook and the raw data form (Section 23.1.).

14.6. Initiate the sequence.

14.7. Data Interpretation

14.7.1. Instrument detector response factor (RF) is in micrograms of carbon per thousand area counts.

14.7.2. Quantitation of the target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the RF readings in the sample and the calibration standards.

14.7.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak can be determined.

14.7.2.2. Determine the TOC concentration of a sample based on the difference in the TC and TIC concentrations obtained from the sample.

14.7.2.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze to maintain the carbon concentration within the 1000ppm carbon range for high level samples or 20ppm for low level samples.

15. CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{M}{A_s - A_b} \times 1000$$

where: RF = response factor for TOC being measured.
M = TOC mass of the sample in µg of carbon.
A_s = peak area of the sample in thousand counts.
A_b = peak area of the calibration blank in thousand counts.

15.2. The percent difference of CCV is calculated as follows:

$$\%D = \frac{|C_{prepared} - C_{measured}|}{C_{prepared}} \times 100$$

where: %D = percent difference of TOC in CCV.
$C_{prepared}$ = TOC concentration prepared.
$C_{measured}$ = TOC concentration measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of LCS/LCSD is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of TOC in LCS (or LCSD).
$C_{recovered}$ = TOC concentration recovered.
C_{added} = TOC concentration added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of the MS/MSD is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of TOC in MS (or MSD).
$C_{recovered}$ = TOC concentration recovered.
C_{sample} = TOC concentration in the sample used.
C_{added} = TOC concentration added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = TOC concentration recovered in measurement 1.
C_2 = TOC concentration recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. TOC concentration in the sample is calculated as follows:

$$C = \frac{M}{V} \times DF \times 1000$$

where: C = TOC concentration of the sample in mg/L of carbon.
M = TOC mass of the sample in µg of carbon.
V = volume of the sample in mL.
DF = dilution factor.

15.7. All concentrations shall be reported in mg/L (ppm) of carbon.

15.8. Report total-organic-carbon concentrations which are < 10 mg/L to 2 significant figures, and total-organic-carbon concentrations which are ≥ 10 mg/L to 3 significant figures.

15.9. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix, or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity, and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH-approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended-length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area and causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area

until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD vary depending upon historical data. The upper and lower acceptance limits for %REC of LCS/LCSD are based upon the historical average recovery ± 3S. The RPD of the LCS/LCSD is ≤ 20%. The LCS/LCSD must be within acceptance limits. If the LCS/LCSD is not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only prepared and analyzed when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for MS/MSDs are as follows:

18.3.1. When the %REC of the MS/MSD is at or within the established acceptance limits, and the RPD is ≤ 25%, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. Report total-organic-carbon concentrations which are < 10mg/L to 2 significant figures, and total-organic-carbon concentrations which are ≥ 10mg/L to 3 significant figures.

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader, and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. "Organic Carbon, Total, Method 415.1 (Combustion or Oxidation)," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.2. "5310 B. High-Temperature Combustion Method," Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

22.3. "5310 D. Wet-Oxidation Method," Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Total Organic Carbon Raw Data Form.

Calscience Environmental Laboratories
Total Organic Carbon Raw Data Form

MBMSLCS

Analyte: Total Organic Carbon

Method:_____ MB/LCS/LCSD Batch No.:_____ Date Prepared:_____

Matrix:_____ MS/MSD Batch No.:_____ Date Analyzed:_____

Concentration Units:_____ Instrument Name:_____ Analyst:_____

Work Order Number	CEL I.D. #	Init. Conc.	DF	Final Conc.	RL	Qual	Comments
Method Blank	MB						

QA/QC

Sample Used	Sample Result	Spike Added	MS Result	%REC	MSD Result	% REC	Control Limits	RPD	Control Limits
							75 - 125		0 - 25
Dilution Factors									

LCS		Conc. Added	LCS Result	%REC	LCSD Result	% REC	Control Limits	RPD	Control Limits
Laboratory Control Sample							80 - 120		0 - 20
Dilution Factors									

A copy of the supporting raw data must be attached.

Figure 23.1

Title : **DETERMINATION of 1,2,3-TRICHLOROPROPANE BY PURGE AND TRAP GC/MS**

Document No. : SOP-M389
Revision No. : 3.0
Supersedes : 2.2

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PROPRIETARY INFORMATION STATEMENT

Revision 3.0 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 01/05/15
MANAGEMENT **DATE**

_____ 01-05-15
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. ►Determination of ***1,2,3-Trichloropropane (TCP) by Purge and Trap*** Gas Chromatography / Mass Spectrometry. This is modified method based on EPA 524.2.

2. APPLICABLE MATRICES

2.1. ►This method is applicable to drinking water, ground water and surface water. Although not specifically tested, this method should be applicable to wastewater. Emergent chemical ***1,2,3-Trichloropropane (TCP)*** can be determined by this method.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The linear calibration range for 1,2,3-Trichloropropane (***TCP***) is from 0.005 to 0.100 ug/L. Although similar to USEPA Method 524.2, this method is designed to quantitate ***TCP*** at concentration of 0.005 µg/L. To achieve the required sensitivity, the quadrupole MS was operated in the selective ion monitoring (SIM) mode.

4. SCOPE AND APPLICATION

4.1. ►This method may be used to determine 1,2,3-Trichloropropane (***TCP***) in water at concentration below the quantifiable ranges of USEPA Methods 504.1, 551.1 and 524.2.

4.2. This method is recommended for use by analysts experienced in gas chromatography / mass spectrometry (GC/MS) and in the interpretation of the resulting ion chromatograms and mass spectra. Analysts using this method should also be proficient in the performance of Method 524.2.

5. ►METHOD SUMMARY

5.1. This analysis is performed using purge and trap and GC/MS.

5.2. ***TCP*** is identified by matching the retention time and fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-Trichloropropane-d_5 (***TCP-d_5***) used as the internal standard, which is added at the same concentration to the samples and standards.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and

systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. ►Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

6.3.1. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.3.2. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. ►Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. ►Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.15. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.16. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.17. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.18. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.19. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.20. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.21. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.22. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.23. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.24. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.25. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. INTERFERENCES

7.1. ►Volatile organic compounds that coelute or overlap with ***TCP / TCP-d_5*** and that yield the same fragment ions as ***TCP / TCP-d_5*** can be a major source of error. Due to the extreme sensitivity of this method, even low abundances of these ions can result in severe interference when the interfering compound is present at sufficiently high concentration.

7.2. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.3. Interferences can also occur when "dirty" samples leave residue in the column. The column can be "baked" after such samples. Screening samples prior to analysis can help eliminate such residue.

7.4. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.5. The following provides information regarding possible target analyte anomalies during analytic processing:

7.5.1. Upon transportation and storage, samples risk contamination by diffusion of contaminants through the septum seal, into the sample container. To determine if samples have been adversely affected during field work, storage, or transportation, "trip" and "source" blanks comprised of interferant-free reagent water can be prepared in the laboratory. The trip blank will accompany the sample containers to and from the field where sampling will occur. The source blank is maintained in an ultra-clean refrigeration unit at the laboratory and will be analyzed should the trip blank yield reportable levels of target analytes. Refer to SOP-T011, "Field QA/AC Samples."

7.5.2. When returned with the samples, the trip blank is processed using the same procedures and under the same conditions as the associated samples. A trip blank with reportable levels of target analytes generally indicates a field activity or transport problem that may adversely affect the representativeness of sample. In this case, the source blank is analyzed to ensure that contamination of the trip blank did, in fact, result from the field operations and not from our source reagent water or trip blank preparation.

7.5.3. Best efforts must be taken to maintain the analytical areas free of all contaminants that include target analytes that are common solvents or reagents in other areas of the laboratory. This can be minimized by restricting entry of these solvents or solvent-contaminated items (e.g., laboratory coats) into the VOC laboratory and proper management / maintenance of laboratory ventilation. Keeping the access doors closed and maintaining a positive pressure in the VOC laboratory should minimize entry of airborne contaminants via ventilation.

7.5.4. Other major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should locate and remove the source of contamination before proceeding with calibration and analysis.

7.5.5. Baking out the column between analyses may eliminate some contamination. Replacing the injector liner will reduce the potential for cross-contamination. The front portion of the analytical column may need to be removed in the case of extreme contamination.

7.5.6. Prior to commencing a new sequence, the column and trap should be conditioned at an elevated temperature for at least 10 minutes. Additionally, any autosampler ports that contained excessively contaminated samples should be baked at an elevated temperature prior to the initiation of the purging process.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should

review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Hewlett Packard 6890Series Gas Chromatograph, Agilent 6890Series Plus Gas Chromatograph, or equivalent configured with the following components:

9.2. Purge-and-Trap System: System configured with a purging chamber and the following components:

9.2.1. Purge-and-trap concentrator, Tekmar-Dohrmann Tekmar LSC 3100 Purge and Trap Concentrator, Teledyne Tekmar Atomx Automated VOC Sample Prep System,Tekmar Stratum PTC Purge and Trap Concentrator, or equivalent.

9.2.2. Condition a new trap according to manufacturer's instructions prior to initial use.

9.2.3. Purge-and-trap autosampler, Teledyne Tekmar Atomx Automated VOC Sample Prep System, Teledyne Tekmar SOLATek 72 Multi-Matrix Vial Autosampler, Varian Archon Purge and Trap Autosampler, or equivalent.

9.2.4. Trap packing material, Tenax® GC/Silica Gel/Charcoal adsorbents, Tenax® GC/Silica Gel/Carbosieve™ S-III adsorbents, Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, Carbopack™ C/Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, or equivalent.

9.3. Purge Gas: Helium (He) or Nitrogen (N_2), high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.4. Instrument Software

9.4.1. Requires a PC based data system or equivalent.

9.4.2. Agilent Environmental MSD ChemStation Version E.02 or equivalent.

9.5. Instrument Maintenance and Troubleshooting

9.5.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.5.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.6. Mass Spectrometer: Hewlett Packard 5973 Mass Selective Detector (MSD), Agilent 5973Network Mass Selective Detector (MSD), or equivalent capable of scanning from 35 to 270 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron-impact ionization (EI) mode, and configured with the following components:

9.6.1. Electron-ionization ion source.

9.6.2. Hyperbolic quadrupole mass filter. System must be capable of operating in the SIM mode.

9.6.3. High energy dynode (HED) electron multiplier detector.

9.6.4. PC based data system, Agilent MSD ChemStation or equivalent equipped with NIST mass spectral library.

9.7. Analytical Column: 25-m × 0.2-mm ID, 1.12-µm film thickness, mid-polar, low bleed, wide-bore, capillary, fused silica, J&W Scientific DB-624 or equivalent.

9.8. Carrier Gas: Helium (He), Hydrogen (H_2) or Nitrogen (N_2), high purity (99.995%), compressed, Praxair 4.5 grade or equivalent. Proper selection of carrier gas is dependent on being able to meet all QA/QC parameters. Temperature program, system response and other factors will need to be optimized as appropriate.

9.9. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.9.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.10. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.11. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

10. ►REAGENTS AND STANDARDS

10.1. ***Reagents***

10.1.1. Reagent water, purified and free from ***TCP*** and other interfering contaminants.

10.1.2. Methanol, purge and trap grade.

10.1.3. ***All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. Standards

10.2.1. Pre-certified stock standard solution in sealed glass ampules, containing ***2000 µg/mL of TCP and 1000 µg/mL of TCP-d_5*** are used to prepare working calibration standards.

10.2.2. Working calibration standard solution containing 0.05 ppm of ***TCP*** in methanol is used to prepare calibration standards.

10.2.2.1. Inject appropriate volume of ***0.05-ppm*** working calibration standard into 25 mL of reagent water, and purge and trap for initial calibration.

10.2.3. Calibration Standards preparation:

10.2.3.1. Use the following calibration levels as guidance to prepare the calibration standards.

Analyte	Standard Compound Concentration (ppb)				
123-TCP	0.005	0.01	0.02	0.05	0.10
123-TCP-d5 (IS)	0.04	0.04	0.04	0.04	0.04

10.2.3.2. The ***midpoint standard is*** also used as the continuing calibration verification ***solution***.

10.2.4. ***Pre-certified stock standard containing*** 1,2,3-Trichloropropane-d_5 at 1000 µg/mL concentration is used to make working ***IS*** solution in methanol for spiking to all the samples and QC samples including MB before analysis.

10.2.4.1. ***Internal standard*** working standard solution containing 1.0 ppm of ***TCP-d_5*** (IS) is prepared in methanol.

10.2.4.2. If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the 1.0 ppm internal standard working standard into each 25-mL aliquot of sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction. If autosampler is <u>not</u> capable to add automatically inject manually.

10.2.4.3. Internal standards concentration in the aqueous working sample is 0.040 µg/L for ***TCP-d_5***.

10.2.5. Initial calibration verification (ICV) solution containing the 0.020 ppb concentration of TCP target analyte and 0.040 ppb of ***TCP-d_5*** in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration.

10.2.5.1. Add the appropriate volumes of the second source working standards and the appropriate volume of the surrogate and internal standard working standard to 25 mL of reagent water, and purge and trap for initial calibration verification.

10.2.5.2. Use the following calibration level as guidance to prepare the ICV solution.

Analyte	ICV Concentration in ppb
TCP	0.02
TCP-d5 (IS)	0.04

10.2.6. Continuing calibration verification (CCV) solution containing the 0.02 µg/L concentration of ***TCP*** analyte and 0.040 ppb of ***TCP-d_5*** in reagent water.

The CCV solution must be of a source same that used for the initial multi-point calibration.

10.2.6.1. Add the appropriate volumes of the working standards and the appropriate volume of the surrogate and internal standard working standard to 25 mL of reagent water, and purge and trap for continuing calibration verification.

10.2.6.2. Use the following calibration levels as guidance to prepare the CCV solutions.

Analyte	CCV Concentration in ppb
TCP	0.02
TCP-d5 (IS)	0.04

10.2.6.3. ***Daily one CCV analyzed at the beginning and one before end of the sequence (ending CCV).***

10.2.7. ***Tuning standard solution contains 25 ppm of 1-bromo-4-fluorobenzene (BFB) in methanol.***

10.2.8. Refer to Appendix A for additional standards.

10.2.8.1. All working standards must be replaced after six months (unless specified otherwise) or sooner if comparison with check standards indicates a problem.

10.2.8.2. Store all working standards with minimal headspace under dark and refrigerated condition.

10.2.8.3. Check all working standards frequently for signs of degradation or evaporation.

10.2.8.4. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.8.5. Check all opened stock standards frequently for signs of degradation or evaporation.

10.2.9. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Collect samples in duplicate in 40-mL amber VOA vials as described in USEPA Method 524.2.

11.2. If the samples contain residual chlorine, add 25 mg of ascorbic acid to each vial before sample collection.

11.3. Store samples at ***0–6°C*** until analysis. Protect samples from direct sunlight or other bright light sources. The sample storage area must be free from organic solvent vapors.

11.4. All samples must be analyzed within 14 days of collection.

12. ▶QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the following acceptance criteria:

12.1.2. The following criteria must be demonstrated every ***24*** hours.

m/z	Relative Abundance Criteria
50	15 – 40% of m/z 95
75	30 – 80% of m/z 95
95	Base peak, 100% relative abundance
96	5 – 9% of m/z 95
173	< 2% of m/z 174
174	> 50% of m/z 95
175	5 – 9% of m/z 174
176	> 95% but < 101% of m/z 174
177	5 – 9% of m/z 176

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action and re-tune the system.

12.2. Initial Calibration (IC)

12.2.1. The initial ***five-point*** calibration must be established prior to the processing of samples.

12.2.1.1. The calibration curve is established with ***five*** calibration standards.

12.2.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.3.1. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis.

12.2.3.2. If one or more analytes do not meet the %RSD, criteria, perform instrument maintenance and recalibrate.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D is ≤ ***20%.***

12.3.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration).

Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and ***at the end of the run sequence***.

12.4.2. The initial calibration is deemed valid if the following conditions are met.

12.4.2.1. The %D for ***TCP*** is ≤ ***20%***.

12.4.3. ***The absolute area of the quantitation ion of TCP-d_5 in the MB, LCS, and CCV should not have decreased by more than 20% from the initial calibration. If necessary make appropriate adjustments to restore system sensitivity.***

12.4.4. ***During the continue calibration verification, verify that the retention times have not drifted from those set in the initial calibration.***

12.4.5. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

12.4.6. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. ***Before processing samples, a MB (LRB) must be analyzed to demonstrate that all the glassware and reagents are free of interfering contaminants. A MB must be analyzed with each batch of 10 samples, or less, or when reagents are changed.***

12.5.2. ***Each day that samples are analyzed, a LCS (LFB) must be analyzed with each batch of 10 samples, or less with a TCP concentration at 0.005 µg/L. The acceptance criteria for LCS TCP recovery as follows:***

12.5.2.1. The lower and upper acceptance limits for %REC of TCP should be between 80% and 120%, respectively. The RPD is ≤ 20%.

12.5.2.2. All LCS/LCSD compounds must be within acceptance limits.

12.5.3. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and re-analyzed.

12.6. Matrix Based Quality Control (***Duplicate***)

12.6.1. ***For batch of 10 samples or less, analyze at least one sample in duplicate if there is a sufficient sample volume to perform the duplicate analysis.***

12.6.2. ***Monitor the integrated areas of TCP-d_5 response during the day and if decreased by more than 20% from the initial calibration, make appropriate adjustments to restore system sensitivity. Re-analyze samples not passing response after system back to normal.***

12.7. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Prior to initial calibration and the analysis of field or QC samples, the GC/MS system must be hardware tuned such that the analysis of 25 ng or less of BFB meets the tuning criteria. The acceptance criteria for the tune are listed in Section 12.1.

13.1.1. Obtain the mass spectrum of BFB as follows:

13.1.1.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of BFB.

13.1.1.1.1. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

13.1.1.1.2. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

13.1.2. All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.

13.1.3. Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.

13.2. Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.1.1. Recalibration is required for the following maintenance procedures.

13.2.1.1.1. Change, replace, or reverse the analytical column.

13.2.1.1.2. Replace the trap on a purge-and-trap system.

13.2.1.1.3. Change the entrance lens, draw-out lens, or repeller.

13.2.1.1.4. Change the electron multiplier and/or ion source chamber.

13.2.1.1.5. Clean the ion source and/or quadrupole rods.

13.2.2. After obtaining an acceptable ***five-point*** calibration curve and prior to processing field or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. ▶PROCEDURE

14.1. Instrument Setup

14.1.1. Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.

14.1.2. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Mode	Split
Inlet initial temp	250°C
Split flow	8.0 mL / min
Inlet pressure	30.24 psi
Total flow rate	11.4 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to 130°C at 9.00°C/min 130°C to 240°C at 45.00°C/min
Run time	17.0 min
Transfer line temperature	280°C
SIM parameters	
Group 1	1
Group ID	High
Ions/Dwell	75/20
Ions/Dwell	79/20
Ions/Dwell	110/20
Ions/Dwell	112/20
Ions/Dwell	114/20
Ions/Dwell	116/20

14.1.3. Following P & T operating conditions as guidance for running this method.

Valve Oven Temp:	150°C	Sample Preheat Time:	1.00 min
Dry Purge Temp:	***40.0°C***	Bake Time:	***4.00 min***
Transfer Line Temp:	150°C	Sample Temp:	40.0°C
Dry Purge Flow:	150 ml/min	Bake Temp:	280°C
Sample Mount Temp:	90.0°C	Purge Time:	11.0 min
GC Start:	Start of Desorb	Bake Flow:	***400.0 ml/min***
Purge Ready Temp:	40.0°C	Purge Temp:	0.0°C
Desorb Preheat Temp:	245°C	Condenser Bake Temp:	***200°C***
Standby Flow:	0.0 ml/min	Purge Flow:	40 ml/min
Desorb Drain:	On	Focus Temp:	-150°C
Pre-Purge Time:	0.50 min	Condenser Ready Temp:	40.0°C
Desorb Time:	***4.00 min***	Inject Time:	1.00 min
Pre-Purge Flow:	40 ml/min	Condenser Purge Temp:	***40.0°C***
Desorb Temp:	250°C	Inject Temp:	180° C
Sample Heater:	Off	Dry Purge Time:	***3.00 min***
Desorb Flow:	***500 ml/min***	Standby Temp:	100°C

14.2. Prepare a 25-mL sample aliquot for analysis as in method 524.2, but use ***TCP-d_5*** as the internal standard.

14.3. ***TCP*** is identified by matching the retention time and fragment ions and ion abundances from the sample with those of the reference standard. Identification requires expert judgment, especially when sample components are not completely resolved, or if ***TCP*** is present at very low concentration (near the detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve.

14.3.1. Quadrupole MS: Calculate the mean abundance ratio of the m/z 75 ion to the m/z 110 ion of ***TCP*** from the initial calibration data. Calculate and compare the abundance ratio of the sample with the reference mean value. The abundance ratio of the sample should compare within ± 30% of the reference mean value.

14.4. Monitor the absolute area of the m/z 79 quantitation ion of the ***TCP-d_5*** in samples. A significant increase in area may signify the additive effect of an m/z 79) from coeluting compounds.

14.4.1. If using the quadrupole MS detector and only the m/z 79 quantitation ion was measured for ***TCP-d_5***, examine the ***TCP-d_5*** peak shape in the EICP and the TIC for possible coeluters, or perform a sample duplicate (a high ***TCP-d_5*** response due to contribution from an interfering compound will result in a calculated ***TCP*** recovery that will be lower than normal).

14.4.2. Take appropriate corrective action, as necessary, to correct for interfering compounds.

14.5. Prior to the analysis of samples or QC samples, the GC/MS system must be hardware tuned and an initial five-point calibration established. The acceptance criteria for the parameters are listed in Section 13.

14.6. To verify the calibration, after obtaining an acceptable five-point calibration curve and prior to processing samples, an initial calibration verification (ICV) must be analyzed to verify the initial calibration standards. The ICV shall be at mid-concentration of the

calibration containing all target analytes and shall be of a source other than that of the initial calibration. The acceptance criteria for the ICV are listed in Section 13.

14.7. The initial five-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14.8. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and ***at the end of the run sequence***.

14.9. At the time of loading samples, the pH condition of each aqueous sample must be measured with narrow range pH paper to determine if the pH of the sample is < 2. The pH range (< 2 or ≥ 2) of each sample shall be documented in the appropriate location on the raw data sheet.

14.10. Following purge-and-trap preparation by the method specified in Section 5.2., the QC and actual environmental samples are received in purge vessels. The purge vessels are then loaded onto the purge-and-trap system.

14.11. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) ***Samples (up to 10 per batch, excluding QC check samples and MBs)***
7) ***Sample Duplicate***
8) ***Samples (up to 10 per batch, excluding QC check samples and MBs)***
9) ***Sample Duplicate***
10) ***Ending CCV***

14.11.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.11.2. Items 2 ***and 10***: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis and ***at the end of the run sequence***.

14.11.3. Item 3: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.11.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water.

14.11.3.2. One LCS is required every day preparatory methods (i.e., purge-and-trap extractions, etc.) are performed for every batch of 20

samples per matrix or portion thereof, whichever is more frequent.

14.11.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section ***15.6.***

14.11.5. Item ***5***: The MB is a known matrix similar to the samples being analyzed that is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (i.e., internal standards, etc.).

14.11.5.1. For aqueous samples, the MB consists of reagent water.

14.11.5.2. A MB is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs may be placed in the sequence.

14.11.6. Items ***6 and 8***: Up to10 samples per batch.

14.11.7. ***Items 7 and 9: The Sample Duplicate is an actual sample analyzed twice using exactly same dilution.***

14.11.7.1. ***The purpose of a Sample Duplicate is to assess the reproducibility of a sample analysis by laboratory.***

14.12. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.13. Initiate the sequence.

14.14. Data Interpretation

14.14.1. The qualitative identification of analytes determined by this method is based on the 1) elution of the sample component at the same relative retention time (RRT) as the standard component and 2) comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.14.2. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.14.2.1. If the %RSD of the target analyte's relative response factor is ≤ ***20%***, then the concentration may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating RF_{ave} is listed in Section 15, Calculations.

14.14.2.2. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided in the below subsections are for the purpose of understanding and data system programming.

14.14.2.2.1. The concentration of the analyte in an aqueous sample is calculated using the concentration of the internal standard in the sample and the purge volume or sample weight, respectively. The formula for calculating the concentration is listed in Section 15, Calculations.

15. CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{(A_x \times C_{is})}{(A_{is} \times C_x)}$$

where:
RF = response factor for target analyte being measured.
A_x = area of the characteristic ion for target analyte being measured.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_{is} = concentration of the specific internal standard in ng/µL.
C_x = concentration of the target analyte being measured in ng/µL.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where:
%RSD = percent relative standard deviation.
SD = standard deviation of the average RFs for the target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The percent difference of each CCC is calculated as follows:

$$\%D = \frac{(C_I - C_c)}{C_I} \times 100$$

where:
%D = percent difference (or percent drift) of CCC.
C_I = CCC standard concentration.

C_c = measured concentration.

Note: Concentrations must be in equivalent units.

15.4. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. The relative percent difference is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. Target analyte concentration in the extract is calculated as follows:

$$C_{ex}\ (mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times RF_{ave})}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the specific internal standard in ng/µL.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of 5 initial RFs for a compound.

15.8. Target analyte concentration for aqueous samples is calculated as follows:

$$C_A\ (\mu g / L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where: C_A = concentration of the target analyte in the aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = extract volume in ml.
V_o = volume of aqueous sample extracted in L.

15.9. Target analyte concentration for solid (or oil) samples is calculated as follows:

$$C_s\ (\mu g / kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where: C_s = concentration of the target analyte in the solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = extract volume in ml.
W_s = weight of solid sample extracted in kg.

15.10. ►Calculate the ***TCP*** sample concentration, using the multipoint calibration established in Section ***10***.

$$C_{TCP} = A_{TCP} Q_{TCP\text{-}d5} / A_{TCP\text{-}d5} (RF_{mean})$$

where:

C_{TCP} = concentration of ***TCP*** in ng/L in the water sample
A_{TCP} = integrated abundance of the m/z 75 quantitation ion for ***TCP***.
$A_{TCP\text{-}d5}$ = integrated abundance of the m/z 79 quantitation ion for the internal standard, ***TCP-d_5***.
$Q_{TCP\text{-}d5}$ = concentration of the internal standard, ***TCP-d_5***, in ng/L.
RF_{mean} = mean response factor of analyte from the initial calibration.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization", shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

16.4. GC/MS-quadrupole (System 1 in Table 1): Single laboratory, single operator.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. ►Material Safety Data Sheets (MSDSs) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated

samples are not detected, the sample data can be reported without qualification.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criterion for MBs is as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2.3. If methylene chloride is found in the MB, no positive sample results should be reported unless the concentration of the compound in the sample exceeds 10 times the MB level. Report the data with qualification indicating the analyte was present in the corresponding MB.

18.3. Additional information regarding internal quality control checks is provided in SOP-T020.

18.4. All concentrations shall be reported in ug/L (ppb) for water samples and ug/kg (ppb) for oil, soil and solid waste samples.

18.5. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An immediate action is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A long-term action is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation

process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. ►Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that

analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Eurofins Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. US EPA, Methods for the Determination of Organic Compounds in Drinking Water Supplement III, (Methods 504.1, 524.2, 551.1) EPA 600/R-95/131, August 1995

22.2. California Department of Health Services, Division of Drinking Water Management, Sanitation and Radiation Laboratories Branch, SRL 524M-TCP February 2002

23. ►APPENDICES, TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. None.

24. MODIFICATIONS

24.1. The following modifications from SRL 524M-TCP are noted.

Calscience SOP M389 Section	Reference Document SRL 524M-TCP Section	Summary of Modification
All	All	None.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
2.2	SOP updated. Section 1: Added two compounds. Section 6.0: Added LOD, LOQ. Section 9.2 and 9.3: Inserted instrument software version & maintenance information Section 10: Added extensive material Section 10: Updated to reflect new surrogate, additional compounds and tuning procedure. Section 12.1.2: BFB criteria changed as EPA 524. Section 12.3.1: ICV %D changed. Section 12.4.2.1: CCV % D changed. Section 14 Added extensive material Section 24: Modifications section added. Section 25: Add revision history.	Y. Patel	2013-02-18
3.0	SOP updated.	Y. Patel	2015-01-09

APPENDIX C

Electronic Data Deliverable Format

Appendix C
Electronic Format for Laboratory Deliverables
Omega Superfund Site Operable Unit 2

Format Name: ddms EFWEDD
Format Version: 1.12
Last Updated 10/15/2015

File Naming Rules:
Data deliverable ZIP file must include the project number, SDG number, and revision number (if applicable). If project number is unknown, contact your ddms project representative.
- FORMAT: [ddms project number]-[SDG number]-[submittal version].zip
- Examples of acceptable file names: 15470000-1234567-1.zip, 15470000F-SDG123-v2.zip

Individual EDD data tables in the deliverable should be saved as text files
- Comma or tab delimited text file (*.csv or *.txt)
- Naming format: table name & extension only: EFW2Sample.txt, EFW2LabTST.txt, EFW2LabRES.txt, and EFW2LabBCH.txt

EDD deliverable must be checked by EDP before submittal. The summary error report needs to be included in the deliverable.
Supporting documentation such as PDF lab reports may be included in the zip file.

Table Rules:
Column Names must be included in each table as the first row of data.
In the column name row, add # character at the start of the row to indicate it is a comment row. (eg. #sys_sample_code...)
All table data, including numeric data, should be in quotes (eg. "MW-1-20140101","","WG","N","","12345"…)

Data Rules:
Non project-specific samples (eg. MS/MSD spiked samples from a different project) should NOT be included in the EDD, even if referenced in the lab report.
EDD values must be consistent with the hard-copy report.
Note on field requirements: ALL fields where data is available should be populated, not only those marked as required.

Column Name Key:
Primary Key (bold red text, underline)
Required (bold red text)
Required in certain circumstances (orange text)
Non-required field (black text)

Version Change Log:

1.12:
- file name examples corrected (minor)
- final_volume, subsample_amount defined format requirements (value must be numeric)

1.11:
- file naming format finalized
- field lengths extended (fsample: collection_quarter, sample_name, sampling_company_code; RES: lab_qualifiers, result_comment)
- sample_type_code requirements note added (Note that for field duplicate samples where the parent is unknown, the sample_type_code used should be "N".)
- field lengths shortened (tst: basis, test_type; RES: detect_flag, level_validated, prevalidation_result, test_type)
- field corrected (PreValdation_Result --> PreValidation_Result)
- Organic_yn changed from Yes/No to Y/N

1.10:
- rule addition: all fields where data is available should be populated, not just those listed as required
- Add to required fields: SMP: depth_unit (conditionally required); sample_date, sample_time, sampling_company_code (conditionally required to required)
- Remove from required fields: SMP: sample_delivery_group
- Extensive description language updates
- TST conditionally required additions: prep_time, leachate_time
- field length extended (RES detect_flag)
- field type changed (reporting_detection_limit changed from numeric to text)
- RES conditionally required additions: detection_limit_unit, lab_qualifiers, qc_dup_original_conc, qc_dup_spike_status, qc_original_conc, qc_rpd, qc_rpd_cl, qc_rpd_status, qc_spike_lcl, qc_spike_status, qc_spike_ucl, result_error_delta, tic_retention_time)
- RES required additions: result_value, source_code
- organic_yn and detect_flag changed from Y/N to Yes/No

Appendix C
Electronic Format for Laboratory Deliverables
Omega Superfund Site Operable Unit 2

Field Name	Data Type	Key	Required	Parent Field	Lookup/ Valid Value	Description	Requirements
sys_sample_code	Text(40)	PK	Y		N	Unique sample identifier.	Each sample, including field and laboratory QC samples, must have a unique value. Sys_sample_code values for normal field samples should match the sample name provided on the COC.
sample_name	Text(50)				N	Additional sample identification as necessary.	Not required to be unique.
sample_matrix_code	Text(10)		Y		Y	Code describing the matrix of the sample as received. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g. leachates), therefore, the matrix is populated in the sample and test tables.	Normal field sample matrix codes values include WG (groundwater) and SO (soil). QC samples include values such as WQ and SQ. See reference table for complete list of valid values. Field blank samples, spiked field samples (sample types MS/MSD) and all laboratory QC samples should have a QC matrix code. Normal field samples and field duplicates should not have a QC matrix code.
sample_type_code	Text(10)		Y		Y	Code which distinguishes different types of samples.	See reference table for complete list of valid values. Example: Normal field samples (sample_type_code = "N") are distinguished from field duplicate samples (sample_type_code = "FD"). Note that for field duplicate samples where the parent is unknown, the sample_type_code used should be "N".
sample_source	Text(10)		Y		Y	This field identifies where the sample came from, either Field or Lab.	Lab-sourced samples include laboratory QC (MB, LCS, LCSD, etc.) and should be listed as 'Lab'. Field-sourced samples include normal samples, field QC (FB, TB, EB, RB) and spiked field samples (MS, MSD) and should be listed as 'Field'.
parent_sample_code	Text(40)		*	EFW2FSample.sys_sample_code	N	The value of "sys_sample_code" that uniquely identifies the sample that was the source of this sample. The value of this field for a duplicate sample would identify the normal sample of which this sample is a duplicate.	Required for all laboratory-created "clone" samples (spikes and duplicates). For example, required where sample_type_code = FD, MS, MSD, LCSD, SD, LR Field must be null for samples which have no parent (for example, normal field samples, LCS samples, method blanks). This includes blind field duplicates where sample type listed as a normal sample.
sample_delivery_group	Text(20)				N	Field sample delivery group. NOT the same as the laboratory sample delivery group.	Leave as null. Laboratory SDG should be populated in EFW2LabTST.lab_SDG
sample_date	Date		Y		N	Date sample was collected in the field.	Required for all samples, including lab QC. "MM/DD/YYYY" format. For field-sourced samples, sample_date should match the date on the COC. For lab-sourced samples, sample_date should equal the prep_date field if not null, or equal the analysis_date if prep_date is not available.

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sample_time	Time		Y		N	Time sample was collected in the field.	Required for all samples, including lab QC. "hh:mm:ss" format. sample_time should match the time on the COC for all field-sourced samples. Sample_time should equal the prep_time field if not null, or equal the analysis_time if prep_time is not available.
sys_loc_code	Text(20)		Y		N	Sample collection location. The SYS_LOC_CODE entered must be identical to the location in the database. If it is not, errors will occur during the commit process. (i.e. MW-1 is not the same as MW1)	QC samples: "Lab QC" or "Field QC" are valid locations. Field samples: use location ID if specified. As most location IDs are unknown to the lab, can use "UNKNOWN".
start_depth	Numeric				N	Beginning depth (top) of soil sample.	Populate where known.
end_depth	Numeric				N	Ending depth (bottom) of soil sample.	Populate where known.
depth_unit	Text(15)		*		Y	Unit of measurement for the sample begin and end depths.	Required if depth fields are populated.
chain_of_custody	Text(40)				N	Chain of custody identifier.	Leave as null.
sent_to_lab_date	Date				N	Date sample was sent to lab.	Date should match date on chain of custody. "MM/DD/YYYY" format.
sample_receipt_date	Date		*		N	Date that sample was received at laboratory.	Required for all field samples. Date should match receipt date listed on chain of custody. "MM/DD/YYYY" format.
sampler	Text(50)				N	Name or initials of sampler.	
sampling_company_code	Text(20)		Y		N	Name or initials of sampling company or, for QC samples, laboratory that generated the sample.	See rt_company reference table for valid values. Populate for field samples based on chain of custody or information provided in the sampling plan. Populate for laboratory samples with the laboratory name code.
sampling_reason	Text(30)				N	Reason for collecting the sampling.	
sampling_technique	Text(40)				Y	Sampling technique.	See reference table for complete list of valid values.
task_code	Text(40)				N	Code used to identify the task under which the field sample was retrieved.	Populate where known.
collection_quarter	Text(6)				N	Quarter of the year sample was collected.	Format should follow quarter-year format. For example, "1Q14" for the first quarter of 2014.
composite_yn	Text(2)				Y	Indicate whether a sample is a composite sample.	Populate where known, "Y" or "N". Most soil/solid samples should have this information provided. May be included on chain of custody or is stated in sampling plan.
composite_desc	Text(255)				N	Description of composite sample (if composite_yn is yes).	
sample_class	Text(10)				N	Sample class code, as defined by the project sampling plan.	
custom_field_1	Text(255)				N	Custom sample field, use as defined by the project sampling plan.	
custom_field_2	Text(255)				N	Custom sample field, use as defined by the project sampling plan.	

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custom_field_3	Text(255)				N	Custom sample field, use as defined by the project sampling plan.	
comment	Text(255)				N	Sample comments as necessary.	
sample_receipt_time	Time				N	Time of lab receipt sample.	"hh:mm:ss" format. If no time available, leave as null.
Source_code	Text(255)		Y	Source_v1.source_code	N	The source file name of the EDD.	Source_code value should match the full zipped file name formatted with file name and extension (eg. "15470000-1234567-1.zip"). Value must be consistent with parent field (Source_v1 table).

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sys_sample_code	Text(40)	PK	Y	EFW2FSample.sys_sample_code EFW2LabSMP.sys_sample_code	N	Unique sample identifier.	Value must be consistent with parent field (EFW2FSample table).
lab_anl_method_name	Text(20)	PK	Y		Y	Laboratory analytic method name or description.	See reference table for complete list of valid values.
analysis_date	Date	PK	Y		N	Date of sample analysis. May refer to either beginning or end of the analysis as required by sample plan.	"MM/DD/YYYY" format.
analysis_time	Time	PK			N	Time of sample analysis. Time zone and daylight savings must be same as analysis_date.	"hh:mm:ss" format.
total_or_dissolved	Text(10)	PK	Y		Y	Result fraction specified in the sampling plan.	Standard values are "T" for total concentration, "D" for dissolved concentration, and "N" for not applicable.
column_number	Text(2)	PK	Y		Y	Column used by laboratory.	Valid values are "NA" for not applicable or not required (most common), "1C" for first column analysis, and "2C" for second column analysis. If "2C"
test_type	Text(10)	PK	Y		Y	Type of test in the laboratory. This field is used to distinguish between initial runs, re-extractions, reanalysis and dilutions.	See reference table for complete list of valid values. Field should reflect the true test run; do not default to "initial" if multiple runs are analyzed.
lab_matrix_code	Text(10)		Y		Y	Code which describes the matrix as analyzed by the lab. May differ from sample_matrix_code.	See reference table for complete list of valid values. In most cases, lab matrix will equal sample matrix. An example of where this would not be true is for Leached samples (leachate lab matrix, WL).
analysis_location	Text(2)		Y		Y	Identify where was sample analyzed.	Valid values are "FL" for mobile field laboratory, "LB" for fixed laboratory, and "FI" for field instrument.
basis	Text(5)		*		Y	Identify the wet or dry basis for reporting.	REQUIRED for soil/solid samples. Valid values are "Wet" for wet weight reporting, "Dry" for dry weight reporting, and "NA" or a null field where the basis is not applicable. Water samples must be reported as null or "NA".
container_id	Text(30)				N	Sample container identifier.	This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
dilution_factor	Numeric		Y		N	Dilution factor at which the analyte was measured effectively.	If sample was not diluted, enter "1".

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lab_prep_method_name	Text(20)		Y		Y	Laboratory sample preparation method code.	See reference table for complete list of valid values. If prep is part of the analytic method, use "METHOD". If no prep, use "NONE". Otherwise, list specific prep method.
prep_date	Date		*		N	Date of sample preparation.	REQUIRED if prep method is not "METHOD" or "NONE". "MM/DD/YYYY" format.
prep_time	Time		*		N	Time of sample preparation. Time zone and daylight savings must be same as analysis_date.	REQUIRED if prep method is not "METHOD" or "NONE". "hh:mm:ss" format.
leachate_method	Text(15)		*		N	Laboratory leachate generation method name or description.	REQUIRED if sample was leached for test. No reference table exists for valid values, but the project manager may specify format used.
leachate_date	Date		*		N	Date of leachate preparation.	REQUIRED if sample was leached for test. "MM/DD/YYYY" format.
leachate_time	Time		*		N	Time of leachate preparation. Time zone and daylight savings must be same as analysis_date.	REQUIRED if sample was leached for test. "hh:mm:ss" format.
lab_name_code	Text(20)		Y		Y	Unique identifier of the laboratory.	See reference table for complete list of valid values.
qc_level	Text(10)				N	Quality control level of analysis.	Default value should be "QUANT" (for quantitative analysis)
lab_sample_id	Text(40)		Y		N	Laboratory LIMS sample identifier.	If necessary, a field sample may have more than one LIMS lab_sample_id (maximum one per each test event).
percent_moisture	Text(5)		*		N	Percent moisture of the sample portion used in this test; this value may vary from test to test for any sample.	REQUIRED for all samples measured (applies for most solid samples). Water samples should be left as null ("100" is not an acceptable value). Format must be an integer value; for example, report 70.1% moisture as "70.1".
subsample_amount	Text(14)				N	Amount of sample used for test.	Value must be numeric.
subsample_amount_unit	Text(15)				Y	Unit of measurement for subsample amount.	See reference table for complete list of valid values.
analyst_name	Text(30)				N	Name or initials of laboratory analyst.	
instrument_id	Text(50)				N	Instrument identifier.	
comment	Text(255)				N	Comments about the test as necessary.	
preservative	Text(20)				Y	Sample preservative used.	See reference table for complete list of valid values.
final_volume	Text(15)				N	The final volume of the sample after sample preparation. Include all dilution factors.	Value must be numeric.
final_volume_unit	Text(15)				Y	The unit of measure that corresponds to the final_volume.	See reference table for complete list of valid values.
lab_SDG	Text(20)		Y		N	Sample delivery group as defined by the laboratory.	SDG number. Please use consistent formatting.

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Source_code	Text(255)		Y	Source_v1.source_ code	N	The source file name of the EDD.	Source_code value should match the full zipped file name formatted with file name and extension (eg. "15470000-1234567-1.zip"). Value must be consistent with parent field (Source_v1 table).

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sys_sample_code	Text(40)	PK	Y	EFW2LabTST.sys_sample_code EFW2LabSMP.sys_sample_code	N	Unique sample identifier.	Value must be consistent with parent field (EFW2LabTST table).
lab_anl_method_name	Text(20)	PK	Y	EFW2LabTST.lab_anl_method_name	Y	Laboratory analytic method name or description.	Value must be consistent with parent field (EFW2LabTST table).
analysis_date	Date	PK	Y	EFW2LabTST.analysis_date	N	Date of sample analysis. May refer to either beginning or end of the analysis as required by sample plan.	Value must be consistent with parent field (EFW2LabTST table).
analysis_time	Time	PK	Y	EFW2LabTST.analysis_time	N	Time of sample analysis. Time zone and daylight savings must be same as analysis_date.	Value must be consistent with parent field (EFW2LabTST table).
total_or_dissolved	Text(10)	PK	Y	EFW2LabTST.total_or_dissolved	Y	Result fraction specified in the sampling plan.	Value must be consistent with parent field (EFW2LabTST table).
column_number	Text(2)	PK	Y	EFW2LabTST.column_number	Y	Column used by laboratory.	Value must be consistent with parent field (EFW2LabTST table).
test_type	Text(10)	PK	Y	EFW2LabTST.test_type	Y	Type of test in the laboratory. This field is used to distinguish between initial runs, re-extractions, reanalysis and dilutions.	Value must be consistent with parent field (EFW2LabTST table).
cas_rn	Text(15)	PK	Y		Y	Cas Number as specified in the project sampling plan.	See reference table for complete list of valid values.
chemical_name	Text(60)		Y		N	Chemical Name as specified in the project sampling plan.	See reference table for complete list of valid values.
result_value	Text(20)		Y*		N	Result value representing the appropriate number of significant digits.	Results MUST be reported to the proper number of significant digits. Detected results should list result detected; non-detected results should list the appropriate reporting limit (in most cases, this would equal the reporting detection limit, RDL). Result types TRG, TIC, IS, and SC should be reported as measured values where appropriate; result type SUR should be reported as a percentage recovery. Text values are acceptable where appropriate (eg. ">=2000" for Coliform results, ">200" for flash point results). NOTE: result/qualifier requirements modified for co-eluting PCB congeners; co-elutes with higher congener numbers should have result_value left as null. Consult ddms project manager with questions.
result_error_delta	Text(20)		*		N	Error range (+/-) applicable to the result value; typically used only for radiochemistry results.	Required for radiochemistry results or where appropriate. +/- range assumed; list only numeric value with appropriate significant figures.

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result_type_code	Text(3)		Y		Y	Type of result being reported (target analyte, surrogate, etc.)	See reference table for complete list of valid values. Should be either "TRG" for a target or regular result, "TIC" for tentatively identified compounds, "SUR" for surrogates, "IS" for internal standards, or "SC" for spiked compounds.
reportable_result	Text(10)		Y		Y	Reportable status of result. Reportable status is used to determine which of all results for each analysis would be the best, most useable result for reporting.	Every sample/method/CAS/fraction should have only one result (the best result as determined by the laboratory) listed as reportable. Value must be "Yes" for result considered reportable or "No" for other results. For analyses with more than one column result, only one of the column results may be listed as reportable. For samples/methods with multiple analysis runs (eg. initial and dilution), only one of the results may be listed as reportable.
detect_flag	Text(2)		Y		Y	Detection status for the analysis.	Must be either "Y" for a detected analyte or "N" for a non-detect.
lab_qualifiers	Text(20)		*		N	Qualifier flags assigned by the laboratory.	Required where qualifiers are appropriate. Non-detects must include a U qualifier. No numeric qualifiers (other than for PCB co-elutes, see note below) are permitted. See reference table for complete list of valid values. NOTE: result/qualifier requirements modified for co-eluting PCB congeners. Co-elutes with higher congener numbers should have qualifier populated with "C" & the lowest congener number, with no other qualifiers listed. Co-elutes with the lowest congener number would be populated with any appropriate qualifiers based on the result AND would be populated with "C" & the lowest congener number. For example, PCB-56 and PCB-57 are co-eluting congeners. The qualifier for PCB-57 would always be "C56" and the qualifier for PCB-57 would list any appropriate qualifers based on the result plus "C56", like "J C56", "U C56", or "C56" if no other qualifier. Consult ddms project manager with questions.
organic_yn	Text(2)				Y	Organic status of the analyte.	May be either "Y" for organic constituents or "N" for inorganic constituents.
method_detection_limit	Text(20)		*		N	The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is >0 and is determined from the analysis of a sample in a given matrix containing the analyte (EPA definition). A calculated value.	REQUIRED for all results except surrogates. Limits must be reported to the proper number of significant digits.

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reporting_detection_limit	Text(20)		*		N	The limit at which nondetect analytes are to be reported. The concentration level above which results can be quantified with 95% confidence limit. Must reflect conditions such as dilution factors and moisture content. Report as the sample specific detection limit.	REQUIRED for all results except surrogates. Limits must be reported to the proper number of significant digits. Field should represent the reportable limit, so it may equal the method_detection_limit or the quantitation_limit field, depending on project requirements.
quantitation_limit	Text(20)		*		N	Concentration level above which results can be quantified with 95% confidence limit. Must reflect conditions such as dilution factors and moisture content. Report as the sample specific quantitation limit.	REQUIRED for all results except surrogates. Limits must be reported to the proper number of significant digits.
result_unit	Text(15)		Y		Y	Units of measurement for the result unit.	
detection_limit_unit	Text(15)		*		Y	Units of measurement for the detection limits.	REQUIRED for all results except surrogates. detection_limit_unit should be identical to result_unit.
tic_retention_time	Text(8)		*		N	Tentatively Identified Compound (TIC) Retention Time.	REQUIRED where result_type = TIC. Report in decimal format (eg. 12.34).
result_comment	Text(255)				N	Result specific comments.	Note: do not populate with "not detected" or similar statement; this information is explicit elsewhere.
qc_original_conc	Text(14)		*		N	The concentration of the analyte in the original (unspiked) sample.	REQUIRED for non-duplicate spiked results (sample_type_code = BS, LCS, MS); do not populate for spike duplicates or unspiked samples.
qc_spike_added	Text(14)		*		N	The concentration of the analyte added to the original sample.	REQUIRED for non-duplicate spiked results (sample_type_code = BS, LCS, MS) and all non-duplicate surrogates (all sample types); do not populate for spike duplicates or unspiked samples.
qc_spike_measured	Text(14)		*		N	The measured concentration of the analyte.	REQUIRED for non-duplicate spiked results (sample_type_code = BS, LCS, MS) and all non-duplicate surrogates (all sample types); do not populate for spike duplicates or unspiked samples. If compound not detected in the sample, use "0".
qc_spike_recovery	Text(14)		*		N	The percent recovery calculated as specified by the laboratory QC program.	REQUIRED for non-duplicate spiked results (sample_type_code = BS, LCS, MS) and all non-duplicate surrogates (all sample types); do not populate for spike duplicates or unspiked samples. Report as a percentage multiplied by 100 (eg. Report 120% recovery as "120").
qc_dup_original_conc	Text(14)		*		N	The concentration of the analyte in the original (unspiked) sample.	REQUIRED for duplicate spiked results (sample_type_code = BD, LCSD, MSD, SD) and all duplicate surrogates (all sample types); do not populate for non-duplicate spikes or unspiked samples.
qc_dup_spike_added	Text(14)		*		N	The concentration of the analyte added to the duplicate sample.	REQUIRED for duplicate spiked results (sample_type_code = BD, LCSD, MSD, SD) and all duplicate surrogates (all sample types); do not populate for non-duplicate spikes or unspiked samples.

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qc_dup_spike_measured	Text(14)		*		N	The measured concentration of the analyte in the duplicate.	REQUIRED for duplicate spiked results (sample_type_code = BD, LCSD, MSD, SD) and all duplicate surrogates (all sample types); do not populate for non-duplicate spikes or unspiked samples. If compound not detected in the sample, use "0".
qc_dup_spike_recovery	Text(14)		*		N	The duplicate percent recovery calculated as specified by the laboratory QC program.	REQUIRED for duplicate spiked results (sample_type_code = BD, LCSD, MSD, SD) and all duplicate surrogates (all sample types); do not populate for non-duplicate spikes or unspiked samples. Report as a percentage multiplied by 100 (eg. Report 120% recovery as "120").
qc_rpd	Text(8)		*		N	The relative percent difference calculated as specified by the laboratory QC program.	REQUIRED for duplicate samples as appropriate. Report as a percentage multiplied by 100 (eg. Report 30% RPD as "30").
qc_spike_lcl	Text(8)		*		N	Lower control limit for spike recovery.	REQUIRED for all spiked results. Report as a percentage multiplied by 100 (eg. Report 60% LCL as "60").
qc_spike_ucl	Text(8)		*		N	Upper control limit for spike recovery	REQUIRED for all spiked results. Report as a percentage multiplied by 100 (eg. Report 120% UCL as "120").
qc_rpd_cl	Text(8)		*		N	Relative percent difference control limit.	REQUIRED for any duplicate sample. Report as a percentage multiplied by 100 (eg. Report 25% as "25").
qc_spike_status	Text(10)		*		N	Used to indicate whether the spike recovery was within control limits.	REQUIRED to be addressed for all non-duplicate spiked results. Use asterisk character ("*") to indicate failure, otherwise leave blank.
qc_dup_spike_status	Text(10)		*		N	Used to indicate whether the duplicate spike recovery was within control limits.	REQUIRED to be addressed for all duplicate spiked results. Use asterisk character ("*") to indicate failure, otherwise leave blank.
qc_rpd_status	Text(10)		*		N	Used to indicate whether the relative percent difference was within control limits.	REQUIRED to be addressed for all duplicate results (spiked and non-spiked). Use asterisk character ("*") to indicate failure, otherwise leave blank.
Final_Qualifiers	Text(20)		*		N	Used to list final reporting qualifier.	Field should equal lab_qualifiers field for all laboratory-submitted data.
Source_code	Text(255)		Y	Source_v1.source_code	N	Source of data	Source_code value should match the full zipped file name formatted with file name and extension (eg. "15470000-1234567-1.zip"). Value must be consistent with parent field (Source_v1 table).
ValidationDate	DateTime				N	Date data was validated	Laboratory data: leave as null. "MM/DD/YYYY" format
ValidatedBy	Text(50)				N	Person who performed the data validation, usually a 3rd party.	Laboratory data: leave as null.

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Validator_Qualifiers	Text(20)				N	Validator-applied qualifiers.	Laboratory data: leave as null. For validated data: If there is no change in qualifiers from the original lab values, field is left blank; for any change in values, the full updated qualifiers are indicated.
Validation_note	Text(255)				N	Validator comments	Laboratory data: leave as null.
level_validated	Text(20)				N	Level validated	Laboratory data: leave as null.
validated_yn	Text(2)		Y		Y	Validation status of the record.	Laboratory data: populate with "N" Use "Y" if the result has been validated (ValidationDate, ValidationBy, and level_validated should also be populated); use "N" if the result has not been validated.
PreValidation_Result	Text(35)				N	Result prior to modification by validator.	Laboratory data: leave as null. If result value has changed due to validation (eg. A result changed from detect to nondetect at a detection limit different from the original result), the original result value is stored here.

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sys_sample_code	Text(40)	PK	Y	EFW2LabTST.sys_sample_code	N	Unique sample identifier.	Value must be consistent with parent field (EFW2LabTST table).
lab_anl_method_name	Text(20)	PK	Y	EFW2LabTST.lab_anl_method_name	Y	Laboratory analytic method name or description.	Value must be consistent with parent field (EFW2LabTST table).
analysis_date	Date	PK	Y	EFW2LabTST.analysis_date	N	Date of sample analysis. May refer to either beginning or end of the analysis as required by sample plan.	Value must be consistent with parent field (EFW2LabTST table).
analysis_time	Time	PK	Y	EFW2LabTST.analysis_time	N	Time of sample analysis. Time zone and daylight savings must be same as analysis_date.	Value must be consistent with parent field (EFW2LabTST table).
total_or_dissolved	Text(10)	PK	Y	EFW2LabTST.total_or_dissolved	Y	Result fraction specified in the sampling plan.	Value must be consistent with parent field (EFW2LabTST table).
column_number	Text(2)	PK	Y	EFW2LabTST.column_number	Y	Column used by laboratory.	Value must be consistent with parent field (EFW2LabTST table).
test_type	Text(10)	PK	Y	EFW2LabTST.test_type	Y	Type of test in the laboratory. This field is used to distinguish between initial runs, re-extractions, reanalysis and dilutions.	Value must be consistent with parent field (EFW2LabTST table).
test_batch_type	Text(10)	PK	Y		Y	Lab Batch type (Prep, Analysis, Leach).	At a minimum, analysis batches must be reported.
test_batch_id	Text(20)		Y		N	Unique identifier for all lab batches.	Batch ID must be a unique code and not re-used.

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source_code	Text(255)	PK	Y		N	Name of the source file where data is from	Source_code value should match the full zipped file name formatted with file name and extension (eg. "15470000-1234567-1.zip").
source_name	Text(255)				N	Name of the source where data is from	For laboratory data, the source_name would be the SDG number.
source_desc	Text(255)				N	Description of the source file: a sampling event or taask, report title, location/facility name, etc.	
source_provider	Text(50)				N	Organization that created the source of the data.	For laboratory data, the source_provider would be the laboratory name. For historical data from tables this would be the author of the document.
source_type	Text(50)				N	Type of file where data is coming from.	For data submitted in this format from a laboratory, source_type = "ddms EFWEDD v1.12" Other valid types include Historical Map, RI Boring Logs, Historical Report, PDF, etc.
source_date	DateTime				N	Date and time that the source file was created. Especially important for historical data.	"MM/DD/YYYY" format
remark	Text(255)				N	Remarks regarding the source	